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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/04086 <b>(22) International Filing Date:</b> 25 February 1999 (25.02.99)  <b>(30) Priority Data:</b> 09/034,525      3 March 1998 (03.03.98)      US 09/130,270      6 August 1998 (06.08.98)      US 09/170,578      13 October 1998 (13.10.98)      US  <b>(71) Applicant:</b> PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US).  <b>(72) Inventors:</b> NOVICH, Bruce, E.; 1035 Highmont Road, Pittsburgh, PA 15232 (US). WU, Xiang; 5165 Amleth Drive, Gibsonsia, PA 15044 (US).  <b>(74) Agents:</b> SIMINERIO, Andrew, C.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> GLASS FIBER-REINFORCED LAMINATES, ELECTRONIC CIRCUIT BOARDS AND METHODS FOR ASSEMBLING A FABRIC  <b>(57) Abstract</b> <p>The present invention provides reinforced laminates for printed circuit boards having a woven reinforcement fabric of a yarn including E-glass fibers having a coating which is compatible with the polymeric matrix material. The yarn has a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about one gram force per gram mass of yarn evaluated using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge. The laminate has a flexural strength in the fill direction of the fabric greater than about 3 x 10<sup>7</sup> kilograms per square meter (about 42.7 kpsi). The yarn coating can include polyester and a polymer selected from vinyl pyrrolidone polymers, vinyl alcohol polymers, starches and mixtures thereof. Alternatively, the laminate has a coefficient of thermal expansion in the z-direction of less than about 4.5 percent at a temperature of 288 °C.</p>		

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**GLASS FIBER-REINFORCED LAMINATES, ELECTRONIC CIRCUIT  
BOARDS AND METHODS FOR ASSEMBLING A FABRIC**

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**Cross Reference to Related Applications**

This patent application is a continuation-in-part of U.S. Patent Application Serial No. 09/130,270 of B. Novich et al. entitled "Glass Fiber-Reinforced Laminates, Electronic Circuit Boards and Methods for Assembling a Fabric", filed August 6, 1998, which is a continuation-in-part application of U.S. Serial No. 09/034,525 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same" filed March 3, 1998.

This patent application is related to U.S. Patent Application Serial No. \_\_\_\_\_ of B. Novich et al. entitled "Methods for Inhibiting Abrasive Wear of Glass Fiber Strands", which is a continuation-in-part application of U.S. Application Serial No. 09/034,078 filed March 3, 1998; U.S. Patent Application Serial No. \_\_\_\_\_ of B. Novich et al. entitled "Glass Fiber Strands Coated With Thermally Conductive Inorganic Solid Particles and Products Including the Same", which is a continuation-in-part application of U.S. Application Serial No. 09/034,663 filed March 3, 1998; U.S. Patent Application Serial No. \_\_\_\_\_ of B. Novich et al. entitled "Impregnated Glass Fiber Strands and Products Including the Same", which is a continuation-in-part application of U.S. Application Serial No. 09/034,077 filed March 3, 1998; and U.S. Patent Application Serial No. \_\_\_\_\_ of B. Novich et al. entitled "Inorganic Particle-Coated Glass Fiber Strands and Products Including the Same", which is a continuation-in-part application of U.S. Application Serial No. 09/034,056 filed March 3, 1998, each of which has been filed concurrently with the present application.

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### **Field of the Invention**

This invention relates generally to reinforced laminates for electronic circuit boards and, more particularly, to laminates containing woven fabrics of glass fibers having a coating which is compatible with laminate matrix resins and facilitates weaving using modern air jet looms.

### **Background of the Invention**

Electronic circuit boards are typically formed from laminated layers of fabric composed of reinforcing fibers, such as glass fibers, which provide dimensional stability to the board to maintain the integrity of the electronic circuits mounted thereon. Distortion or warpage of the board due to different rates of thermal expansion of board components caused by temperature gradients during fabrication and use can adversely affect adhesion of the circuits to the board, and therefore its reliability and performance.

The smoothness of the surface of the laminate can also affect adhesion of the electronic circuits to the board. Defects in the woven cloth reinforcement, such as broken filaments or fuzz, can adversely affect surface smoothness and inhibit adhesion between the circuits and the laminate. In an air jet loom, fuzz is produced when glass fiber filaments in the bundles are severed when the warp is impacted by the reed or when the weft is blown by the high speed air jet. As the speed of modern air jet looms increases, the strand integrity and resistance to fiber breakage provided by the strand coating becomes more important.

The coating on the glass fibers also influences the quality of the board. Starch, which is a component of many sizing compositions for glass fibers used in weaving operations, can adversely affect adhesion between the glass fibers and the laminate matrix material, i.e., the starch is generally not compatible with the laminate resin matrix material. To avoid incompatibility between the glass fibers and matrix materials, the coating or sizing

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composition is typically removed from the woven cloth prior to lamination by thermally decomposing the components of the sizing (heat treatment or de-oiling) or by washing with water. A conventional heat cleaning process involves heating the cloth at 380°C for 60-80 hours. The cleaned cloth is then  
5 re-coated with a silane coupling agent to improve adhesion between the glass fiber and the matrix resin.

The strength of the glass fibers, and more particularly the flexural strength of the laminate, can be greatly reduced by these thermal fiber coating removal processes. Heat cleaning of high silica content glass fibers,  
10 such as D-glass, S-glass and Q-glass, is particularly undesirable because of strength loss and discoloration.

Many coating compositions for glass fibers which require heat or water cleaning prior to use as a reinforcement in a composite or laminate are disclosed in the art. Japanese Patent Application No. 9-208,268 discloses a  
15 cloth having yarn formed from glass fibers coated immediately after spinning with starch or a synthetic resin and 0.001 - 20.0 weight percent of inorganic solid particles such as colloidal silica, calcium carbonate, kaolin and talc. Heat or water deoiling is required prior to formation of a laminate.

U.S. Patent No. 5,286,562 discloses a textile strand for screen  
20 products which is weavable on air jet looms having a coating of at least 45 weight percent wax, lubricants, polyvinyl pyrrolidone and organo silane coupling agents. U.S. Patent No. 5,038,555 discloses twisted bundles of glass fibers for screen products which are coated with an aqueous chemical treating composition having an epoxy film former, emulsifier, lubricant, organo  
25 functional metallic coupling agent, polyvinyl pyrrolidone, polyethylene and water.

To avoid heat cleaning glass fiber cloth, Japanese Patent Application No. 8-119,682 discloses a primary sizing agent for glass fibers containing a water-soluble epoxy resin and having a pH of 5.5 to 7.5, which facilitates

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removal of the sizing with water. Similarly, U.S. Patent No. 5,236,777 discloses methods for producing glass cloth for reinforcing a resin by coating the glass yarns with a primary sizing having at least one water-soluble film-forming agent selected from the group consisting of an amine-modified epoxy resin, an ethylene oxide-added epoxy resin and ethylene oxide-added bisphenol A, silane coupling agent and lubricant, water washing the yarns to reduce the amount of primary sizing to less than 0.25 weight percent LOI and treating with a secondary sizing agent. Japanese Patent Application No. 9-268,034 discloses binders for twist-free glass fiber yarn including a water-soluble urethane compound and/or a water-soluble epoxy product modified by addition reaction with a polyhydric alcohol.

U.S. Patent No. 4,933,381 discloses a resin-compatible size composition for glass fibers containing an epoxy film-former, non-ionic lubricant, cationic lubricant, silane coupling agent and an acid such as acetic or citric acid.

Japanese Patent Application No. 8-325,950 discloses a glass fiber sizing agent including as essential components polyvinyl pyrrolidone, a water-soluble epoxy resin amine addition product and a silane coupling agent which do not require heat removal from finished glass cloth.

Japanese Patent Application No. 7-102,483 discloses a warp secondary sizing agent for glass fiber for weaving glass cloth that does not require heat oil removal. The warp secondary sizing agent is composed mainly of polyvinyl pyrrolidone and contains an additive such as high molecular weight polyethylene oxide. A water-soluble epoxy resin can be included as a binding component.

There is a need for glass fibers which are compatible with a variety of polymeric matrix materials, which prevent formation of fuzz and fiber breakage during weaving to improve adhesion between the laminate and



circuits, and which are compatible with modern air jet weaving equipment to increase productivity.

### Summary of the Invention

5           One aspect of the present invention is a reinforced laminate for an electronic support, the laminate comprising: (a) a polymeric matrix material; and (b) a woven reinforcement fabric comprising a yarn comprising glass fibers at least partially coated with a coating which is compatible with the polymeric matrix material, the yarn having a loss on ignition ranging from  
10   about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air  
15   pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi).

          Another aspect of the present invention is a reinforced laminate for an electronic support, the laminate comprising: (a) a polymeric matrix material;  
20   and (b) a woven reinforcement fabric comprising a yarn comprising glass fibers at least partially coated with a coating which is compatible with the polymeric matrix material, the coating comprising (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches.

25           Another aspect of the present invention is a reinforced laminate for an electronic support, the laminate comprising: (a) a polymeric matrix material; and (b) a woven reinforcement fabric comprising a yarn comprising glass fibers at least partially coated with a coating which is compatible with the

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polymeric matrix material, the coating comprising (1) polyester; and (2) vinyl pyrrolidone polymer.

Yet another aspect of the present invention is an electronic circuit board comprising: (a) a laminate for an electronic support comprising: (I) a  
5 woven fabric comprising a yarn comprising glass fibers, the yarn having a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a  
10 length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi); and (ii) a layer of a polymeric matrix material  
15 applied over at least a portion of the fabric; and (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the laminate.

Another aspect of the present invention is an electronic circuit board comprising: (a) a laminate for an electronic support comprising: (i) a woven  
20 fabric comprising a yarn comprising glass fibers at least partially coated with a coating comprising (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches; and (ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and (b) an electrically conductive layer positioned  
25 adjacent to selected portions of selected sides of the laminate.

Still another aspect of the invention is an electronic circuit board comprising: (a) a laminate for an electronic support comprising: (i) a first composite layer comprising: (1) a woven fabric comprising a yarn comprising glass fibers, the yarn having a loss on ignition ranging from about 0.01 to

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about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of  
5 about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi); and (2) a layer of a polymeric matrix material applied over at least a portion of the fabric; and (ii)  
10 a second composite layer different from the first composite layer; and (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the laminate.

Yet another aspect of the present invention is an electronic circuit board comprising: (a) a laminate for an electronic support comprising: (i) a  
15 first composite layer comprising: (1) a woven fabric comprising a yarn comprising glass fibers at least partially coated with a coating comprising (A) polyester; and (B) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches; and (2) a layer of a polymeric matrix material applied over at least a portion of the  
20 fabric; and (ii) a second composite layer different from the first composite layer; and (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the laminate.

Another aspect of the present invention is a copper-clad reinforced laminate for an electronic support, the laminate comprising: (a) a polymeric  
25 matrix material; and (b) one or more plies of woven reinforcement fabric, each of the plies comprising between about 30 and about 75 weight percent of yarn comprising glass fibers at least partially coated with a coating which is compatible with the polymeric matrix material, wherein the laminate has a

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coefficient of thermal expansion in the z-direction of less than about 4.5 percent at a temperature of 288°C.

Yet another aspect of the present invention is a method for assembling a fabric by interweaving a first yarn with a second yarn to form a fabric,

- 5 wherein the improvement comprises: the first yarn comprising glass fibers at least partially coated with a coating which is compatible with a polymeric matrix material, the coating comprising: (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers, starches and mixtures thereof.

- 10 Still another aspect of the present invention is a method for forming a laminate of a woven fabric and a polymeric matrix material by at least partially coating the woven fabric with the polymeric matrix material to form a coated fabric and applying heat to the coated fabric, the woven fabric comprising a yarn comprising glass fibers, wherein the improvement comprises: the glass  
15 fibers being at least partially coated with a coating which is compatible with the polymeric matrix material, the yarn having a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter  
20 of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, and the laminate having a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi).

- 25 Another aspect of the present invention is a method for forming a laminate of a woven fabric and a polymeric matrix material by at least partially coating the woven fabric with the polymeric matrix material to form a coated fabric and applying heat to the coated fabric, the woven fabric comprising a yarn comprising glass fibers, wherein the improvement comprises: the glass

fibers being at least partially coated with a coating which is compatible with a polymeric matrix material, the coating comprising: (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches.

5

### **Brief Description of the Drawings**

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. In the drawings:

10        Fig. 1 is a cross-sectional view of a reinforced laminate according to the present invention;

          Fig. 2 is a top plan view of a fabric according to the present invention;

          Fig. 3 is a perspective view of a coated fiber strand according to the present invention;

15        Fig. 4 is a cross-sectional view of an electronic support according to the present invention;

          Fig. 5 is a cross-sectional view of an alternative embodiment of an electronic support according to the present invention;

          Fig. 6 is a schematic diagram of a method for assembling a fabric and  
20        forming a laminate according to the present invention; and

          Fig. 6a is an enlargement of a portion of Fig. 6.

### **Detailed Description of the Invention**

25        The laminates of the present invention are reinforced with woven fabric comprising coated glass fiber strands which can provide the laminate with low coefficient of thermal expansion, good flexural strength, thermal stability, hydrolytic stability, low corrosion and reactivity in the presence of high humidity, reactive acids and alkalies. The coated glass fiber strands are

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compatible with a variety of polymeric matrix materials, which can eliminate the need for heat or water cleaning of the glass fiber fabric prior to lamination.

Another significant advantage of the coated glass fiber strands of the present invention is good processability in weaving and knitting, particularly in  
5 air jet weaving. As used herein, "air jet weaving" means a type of fabric weaving (shown in Fig. 5) in which the fill yarn (weft) is inserted into the warp shed by a blast of compressed air from one or more air jet nozzles. The air jet drag transport force (discussed below) is a measure of compatibility of the strand with the air jet propulsion process. Higher air jet drag force values  
10 indicate that the yarn appropriately filamentizes without breakage and therefore is more aerodynamically conducive to air jet propulsion.

Low fuzz and halos, low broken filaments, low forming package ringers, low bobbin ringers, low strand tension, high reliability and low insertion time are other desirable characteristics which can be provided by the coated  
15 glass fiber strands of the present invention to facilitate weaving and knitting and consistently provide a fabric with good smoothness and few surface defects for printed circuit board applications.

Referring now to the Figures, wherein like numerals indicate like elements throughout, Fig. 1 shows a laminate 10 according to the present  
20 invention. The laminate 10 comprises a polymeric matrix material 12 (discussed in detail below) which is reinforced by a woven reinforcement fabric 14. The fabric 14 can be formed by any suitable knitting or weaving process, but preferably is formed by an air jet weaving process such as is discussed in detail below.

25 Referring now to Figs. 2 and 3, the fabric 14 comprises one or more coated fiber strands 16 comprising at least one glass fiber 18. Preferably the strand 16 comprises a plurality of glass fibers 18. As used herein, the term "strand" means one or more individual fibers. The term "fiber" means an individual filament.

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The glass fibers 18 can be formed from any type of fiberizable glass composition known to those skilled in the art, including those prepared from fiberizable glass compositions such as "E-glass", "A-glass", "C-glass", "D-glass", "Q-glass", "R-glass", "S-glass" and E-glass derivatives. As used  
5 herein, "E-glass derivatives" means glass compositions which include minor amounts of fluorine and/or boron and preferably are fluorine-free and/or boron-free. Furthermore, as used herein, minor means less than about 1 weight percent fluorine and less than about 5 weight percent boron. Basalt and mineral wool fibers are examples of other glass fibers useful in the  
10 present invention. Preferred glass fibers are formed from E-glass or E-glass derivatives. Such compositions and methods of making glass filaments therefrom are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. If additional information is needed, such glass compositions and fiberization  
15 methods are disclosed in K. Loewenstein, The Manufacturing Technology of Glass Fibres, (3d Ed. 1993) at pages 30-44, 47-60, 115-122 and 126-135, U.S. Patents 4,542,106 and 5,789,329, and IPC-EG-140 "Specification for Finished Fabric Woven from 'E' Glass for Printed Boards" at page 1, a publication of The Institute for Interconnecting and Packaging Electronic  
20 Circuits (June 1997), which are hereby incorporated by reference.

The glass fibers can have a nominal filament diameter ranging from about 5.0 to about 35.0 micrometers (corresponding to a filament designation of D through U and above), and preferably have a nominal filament diameter ranging from about 9.0 to about 30.0 micrometers. The number of fibers per  
25 strand can range from about 100 to about 15,000, and is preferably about 200 to about 7000. For further information regarding nominal filament diameters, and designations of glass fibers, see Loewenstein at pages 25 and 27, which are hereby incorporated by reference.

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In addition to glass fibers, the coated fiber strand 16 can further comprise fibers 20 formed from other fiberizable natural or man-made materials, such as non-glass inorganic materials, natural materials, organic polymeric materials and combinations thereof. As used herein, the term  
5 "fiberizable" means a material capable of being formed into a generally continuous filament, fiber, strand or yarn.

Suitable non-glass inorganic fibers include ceramic fibers formed from silicon carbide, carbon, graphite, mullite, aluminum oxide and piezoelectric ceramic materials. Non-limiting examples of suitable animal and vegetable-  
10 derived natural fibers include cotton, cellulose, natural rubber, flax, ramie, hemp, sisal and wool. Suitable man-made fibers include those formed from polyamides (such as nylon and aramids), thermoplastic polyesters (such as polyethylene terephthalate and polybutylene terephthalate), acrylics (such as polyacrylonitriles), polyolefins, polyurethanes and vinyl polymers (such as  
15 polyvinyl alcohol). Non-glass fibers believed to be useful in the present invention and methods for preparing and processing such fibers are discussed at length in the Encyclopedia of Polymer Science and Technology, Vol. 6 (1967) at pages 505-712, which is hereby incorporated by reference. It is understood that blends or copolymers of any of the above materials and  
20 combinations of fibers formed from any of the above materials can be used in the present invention, if desired.

The present invention will now be discussed generally in the context of glass fiber strands, although one skilled in the art would understand that the strand 16 can additionally include one or more of the non-glass fibers  
25 discussed above.

Referring to Figs. 2 and 3, in a preferred embodiment, the fibers 18 of the strand 16 are coated with a layer 22 of a coating composition applied to at least a portion of a surface of the fibers 18 to protect the fiber surface from abrasion during processing and inhibit breakage of the fibers 18. Preferably



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the coating composition is applied to the entire outer surface or periphery of the each of the fiber(s) 18 of the strand 16.

The coating composition can be present upon the fibers as a sizing (preferred), a secondary coating applied over a sizing and/or a tertiary or  
5 outer coating, as desired. As used herein, the terms "size", "sized" or "sizing" refer to the coating composition applied to the fibers immediately after formation of the fibers. In an alternative embodiment, the terms "size", "sized" or "sizing" additionally refer to the coating composition (also known as a  
"finishing size") applied to the fibers after a conventional primary coating  
10 composition has been removed by heat, water or chemical treatment, i.e., a finishing size which is applied to bare glass fibers incorporated into a fabric form. The term "secondary coating" refers to a coating composition applied secondarily to one or a plurality of strands after the sizing composition is applied, and preferably at least partially dried.

15 The coating composition comprises one or more polymeric materials, such as thermosetting materials or thermoplastic materials, which are compatible with the polymeric matrix material 12 of the laminate 10, i.e., the components of the coating composition facilitate wet-out and wet-through of the matrix material upon the fiber strands and provide adequate physical  
20 properties in the composite. Preferably the polymeric materials form a generally continuous film when applied to the surface of the fibers 18. The polymeric materials can be water soluble, emulsifiable, dispersible and/or curable.

In a preferred embodiment, the coating composition comprises one or  
25 more polymeric film forming materials which are compatible with a thermosetting matrix material such as are used to form laminates for printed circuit boards, for example FR-4 epoxy resins, which are polyfunctional epoxy resins and in one particular embodiment of the invention is a difunctional brominated epoxy resins, and polyimides. See 1 Electronic Materials

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Handbook, ASM International (1989) at pages 534-537, which are hereby incorporated by reference. As used herein, the phrase "compatible with a thermosetting matrix material" means that the components of the coating composition facilitate wet-through and wet-out of the matrix material upon the  
5 fiber strands, provide adequate physical properties in the composite, are chemically compatible with the thermosetting matrix material and are resistant to hydrolysis. The measure of the penetration of the polymeric matrix material through the mat is referred to as "wet-through". The measure of the flowability of the polymeric matrix material through the glass fiber mass to  
10 obtain essentially complete encapsulation of the entire surface of each glass fiber by the polymeric matrix material is referred to as "wet-out".

Useful polymeric film forming materials include thermoplastic polymeric materials such as thermoplastic polyesters, vinyl polymers, polyolefins, polyamides (e.g. aliphatic polyamides or aromatic polyamides such as  
15 aramid), thermoplastic polyurethanes, acrylic polymers and mixtures thereof which are compatible with a thermosetting matrix material. Preferred thermoplastic polyesters include DESMOPHEN 2000 and DESMOPHEN 2001KS, both of which are commercially available from Bayer of Pittsburgh, Pennsylvania, and RD-847A polyester resin which is commercially available  
20 from Borden Chemicals of Columbus, Ohio. Useful polyamides include the VERSAMID products which are commercially available from General Mills Chemicals, Inc. Useful thermoplastic polyurethanes include WITCOBOND® W-290H which is commercially available from Witco Chemical Corp. of Chicago, Illinois and RUCOTHANE® 2011L polyurethane latex which is  
25 commercially available from Ruco Polymer Corp. of Hicksville, New York.

Useful thermosetting polymeric materials include thermosetting polyesters, epoxy materials, vinyl esters, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof which are compatible with a thermosetting matrix material. Suitable thermosetting polyesters can

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include STYPOL polyesters which are commercially available from Cook Composites and Polymers of Port Washington, Wisconsin and NEOXIL polyesters which are commercially available from DSM B.V. of Como, Italy.

Useful epoxy materials contain at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols. Examples of suitable epoxy polymers include EPON® 826 and EPON® 880 epoxy resins, which are epoxy functional polyglycidyl ethers of bisphenol A commercially available from Shell Chemical Company of Houston, Texas. Preferably, however, the coating composition is essentially free of epoxy materials, i.e., comprises less than about 5 weight percent epoxy materials and more preferably less than about 2 weight percent.

Preferably, the coating composition comprises one or more polyesters (preferably DESMOPHEN 2000 and RD-847A) and one or more additional film-forming polymers selected from the group consisting of vinyl pyrrolidone polymers (preferred), vinyl alcohol polymers and/or starches. Preferred vinyl pyrrolidone polymers useful in the present invention include polyvinyl pyrrolidones such as PVP K-15, PVP K-30, PVP K-60 and PVP K-90, each of which are commercially available from ISP Chemicals of Wayne, New Jersey. Useful starches include those prepared from potatoes, corn, wheat, waxy maize, sago, rice, milo and mixtures thereof, such as Kollotex 1250 (a low viscosity, low amylose potato-based starch etherified with ethylene oxide) which is commercially available from AVEBE of the Netherlands. The amount of additional polymer is preferably less than about 10 weight percent, and more preferably ranges from about 0.1 to about 5 weight percent. Preferably, the coating composition is essentially free of starch, i.e., contains less than about 5 weight percent starch and more preferably is free of starch, which is often incompatible with the matrix material.

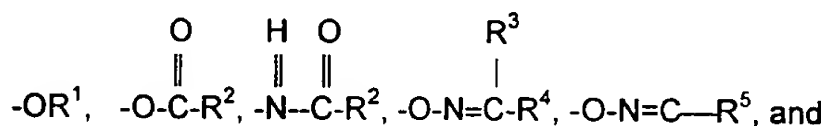
In an alternative preferred embodiment for laminates for printed circuit boards, the polymeric materials of the coating composition comprise a mixture

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of RD-847A polyester resin, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester and VERSAMID polyamide. The coating composition can comprise a mixture of one or more thermosetting polymeric materials with one or more thermoplastic polymeric materials.

- 5 Generally, the amount of polymeric material can range from about 1 to about 99 weight percent of the coating composition on a total solids basis, preferably about 1 to about 50 weight percent and more preferably about 1 to about 25 weight percent.

- 10 In addition to or in lieu of the polymeric materials discussed above, the coating composition preferably comprises one or more coupling agents such as organo silane coupling agents, transition metal coupling agents, phosphonate coupling agents, aluminum coupling agents, amino-containing Werner coupling agents and mixtures thereof. These coupling agents typically have dual functionality. Each metal or silicon atom has attached to it  
15 one or more groups which can react or compatibilize with the fiber surface and/or the components of the coating composition. As used herein, the term "compatibilize" means that the groups are chemically attracted, but not bonded, to the fiber surface and/or the components of the coating composition, for example by polar, wetting or solvation forces. Examples of  
20 hydrolyzable groups include:



- 25 the monohydroxy and/or cyclic C<sub>2</sub>-C<sub>3</sub> residue of a 1,2- or 1,3 glycol, wherein R<sup>1</sup> is C<sub>1</sub>-C<sub>3</sub> alkyl; R<sup>2</sup> is H or C<sub>1</sub>-C<sub>4</sub> alkyl; R<sup>3</sup> and R<sup>4</sup> are independently selected from H, C<sub>1</sub>-C<sub>4</sub> alkyl or C<sub>6</sub>-C<sub>8</sub> aryl; and R<sup>5</sup> is C<sub>4</sub>-C<sub>7</sub> alkylene. Examples of suitable compatibilizing or functional groups include epoxy, glycidoxy, mercapto, cyano, allyl, alkyl, urethano, halo, isocyanato, ureido, imidazoliny, vinyl, acrylato, methacrylato, amino or polyamino groups.
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Functional organo silane coupling agents are preferred for use in the present invention. Examples of useful functional organo silane coupling agents include gamma-aminopropyltrialkoxysilanes, gamma-isocyanatopropyltriethoxysilane, vinyl-trialkoxysilanes, glycidoxypropyltrialkoxysilanes and ureidopropyltrialkoxysilanes. Preferred functional organo silane coupling agents include A-187 gamma-glycidoxypropyltrimethoxysilane, A-174 gamma-methacryloxypropyltrimethoxysilane, A-1100 gamma-aminopropyltriethoxysilane silane coupling agents, A-1108 amino silane coupling agent and A-1160 gamma-ureidopropyltriethoxysilane (each of which are commercially available from OSi Specialties, Inc. of Tarrytown, New York). The organo silane coupling agent can be at least partially hydrolyzed with water prior to application to the fibers, preferably at about a 1:1 stoichiometric ratio or, if desired, applied in unhydrolyzed form.

Suitable transition metal coupling agents include titanium, zirconium, yttrium and chromium coupling agents. Suitable titanate coupling agents and zirconate coupling agents are commercially available from Kenrich Petrochemical Company. Suitable chromium complexes are commercially available from E.I. duPont de Nemours of Wilmington, Delaware. The amino-containing Werner-type coupling agents are complex compounds in which a trivalent nuclear atom such as chromium is coordinated with an organic acid having amino functionality. Other metal chelate and coordinate type coupling agents known to those skilled in the art also can be used herein.

The amount of coupling agent can range from about 1 to about 99 weight percent of the coating composition on a total solids basis, and preferably about 1 to about 10 weight percent.

Referring to Figure 3, in a preferred embodiment of the present invention, the coating composition comprises one or more solid particles positioned between or adhered to the outer surfaces of the fibers 18. If

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positioned between adjacent glass fibers 26, 28 of the strand 16, these solid particles 24 can provide interstitial spaces 30 which correspond generally to the average particle size 32 of the solid particles 24. As used herein, "solid" means a substance that does not flow perceptibly under moderate stress, has  
5 definite capacity for resisting forces which tend to deform it, and under ordinary conditions retains a definite size and shape. See Webster's Third New International Dictionary of the English Language - Unabridged (1971) at page 2169. Furthermore, as used herein, the term "solid" includes both crystalline and non-crystalline materials.

10 The solid particles 24 can have an average particle size 32 (equivalent spherical diameter) ranging from about 0.01 to greater than 5 micrometers, preferably from about 1 to about 1000 micrometers, and more preferably about 1 to about 25 micrometers. Preferably, the minimum average particle size 32 of the solid particles 24 corresponds generally to the average nominal  
15 diameter of the glass fibers.

The configuration or shape of the solid particles 24 can be generally spherical (such as beads, microbeads or solid hollow spheres), cubic, platy or acicular (elongated or fibrous), as desired. For more information on suitable particle characteristics see H. Katz et al. (Ed.), Handbook of Fillers and  
20 Plastics (1987) at pages 9-10, which are hereby incorporated by reference. The solid particles preferably do not crumble, deform or dissolve in the coating composition to a particle size of less than 5 micrometers, and preferably not less than 3 micrometers, under typical glass fiber processing conditions, such as exposure to temperatures of up to about 25 °C, and more  
25 preferably up to about 400°C.

Glass fibers are subject to abrasive wear by contact with asperities of adjacent glass fibers and/or other solid objects or materials which the glass fibers contact during forming and subsequent processing, such as weaving or roving. "Abrasive wear", as used herein, means scraping or cutting off of bits

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of the glass fiber surface or breakage of glass fibers by frictional contact with particles, edges or entities of materials which are hard enough to produce damage to the glass fibers. See K. Ludema, Friction, Wear, Lubrication, (1996) at page 129, which is hereby incorporated by reference. Abrasive

- 5 wear of glass fiber strands causes strand breakage during processing and surface defects in products such as woven cloth and composites, which increases waste and manufacturing cost.

- To minimize abrasive wear, the solid particles have a hardness value which does not exceed, i.e., is less than or equal to, a hardness value of the
- 10 glass fiber(s). The hardness values of the solid particles and glass fibers can be determined by any conventional hardness measurement method, such as Vickers or Brinell hardness, but is preferably determined according to the original Mohs' hardness scale which indicates the relative scratch resistance of the surface of a material. The Mohs' hardness value of glass fibers
- 15 generally ranges from about 4.5 to about 6.5, and is preferably about 6. R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22, which is hereby incorporated by reference. The Mohs' hardness value of the solid particles preferably ranges from about 0.5 to about 6. The Mohs' hardness values of several non-limiting examples of solid particles
- 20 suitable for use in the present invention are given in Table A below.

Table A

Solid particle material	Mohs' hardness (original scale)
boron nitride	about 2 <sup>1</sup>
graphite	about 0.5-1 <sup>2</sup>
molybdenum disulfide	about 1 <sup>3</sup>
talc	about 1-1.5 <sup>4</sup>
mica	about 2.8-3.2 <sup>5</sup>

<sup>1</sup> K. Ludema, Friction, Wear, Lubrication, (1996) at page 27, which is hereby incorporated by reference.

<sup>2</sup> R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22.

<sup>3</sup> R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 793, which is hereby incorporated by reference.

<sup>4</sup> Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 1113, which is hereby incorporated by reference.

<sup>5</sup> Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 784, which is hereby incorporated by reference.

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kaolinite	about 2.0-2.5 <sup>6</sup>
gypsum	about 1.6-2 <sup>7</sup>
calcite (calcium carbonate)	about 3 <sup>8</sup>
calcium fluoride	about 4 <sup>9</sup>
zinc oxide	about 4.5 <sup>10</sup>
aluminum	about 2.5 <sup>11</sup>
copper	about 2.5-3 <sup>12</sup>
iron	about 4-5 <sup>13</sup>
gold	about 2.5-3 <sup>14</sup>
nickel	about 5 <sup>15</sup>
palladium	about 4.8 <sup>16</sup>
platinum	about 4.3 <sup>17</sup>
silver	about 2.5-4 <sup>18</sup>

As mentioned above, the Mohs' hardness scale relates to the resistance of a material to scratching. The instant invention, therefore, contemplates particles that have a hardness at their surface that is different from the hardness of the internal portions of the particle beneath its surface. More specifically, the surface of the particle can be modified in any manner well known in the art, including but not limited to coating, cladding or encapsulating the particle or chemically changing its surface characteristics using techniques known in the art, such that the surface hardness of the particle is not greater than the hardness of the glass fibers while the hardness of the particle beneath the surface is greater than the hardness of the glass fibers. For example but not limiting the present invention, inorganic particles such as silicon carbide and aluminum nitride can be provided with a silica, carbonate or nanoclay coating. In addition, silane coupling agents with alkyl

<sup>6</sup> Handbook of Chemistry and Physics at page F-22.

<sup>7</sup> Handbook of Chemistry and Physics at page F-22.

<sup>8</sup> Friction, Wear, Lubrication at page 27.

<sup>9</sup> Friction, Wear, Lubrication at page 27.

<sup>10</sup> Friction, Wear, Lubrication at page 27.

<sup>11</sup> Friction, Wear, Lubrication at page 27.

<sup>12</sup> Handbook of Chemistry and Physics at page F-22.

<sup>13</sup> Handbook of Chemistry and Physics at page F-22.

<sup>14</sup> Handbook of Chemistry and Physics at page F-22.

<sup>15</sup> Handbook of Chemistry and Physics at page F-22.

<sup>16</sup> Handbook of Chemistry and Physics at page F-22.

<sup>17</sup> Handbook of Chemistry and Physics at page F-22.

<sup>18</sup> Handbook of Chemistry and Physics at page F-22.



side chains can be reacted with the surface of many oxide particles to provide a "softer" surface.

Generally, solid particles 24 useful in the present invention can be formed from inorganic materials, organic materials or mixtures thereof.

5 Preferably, the solid particles 24 are formed from inorganic materials selected from the group consisting of ceramic materials and metallic materials.

Suitable ceramic materials include metal nitrides, metal oxides, metal carbides, metal sulfides, metal borides, metal silicates, metal carbonates and mixtures thereof.

10 A non-limiting of a suitable metal nitride is boron nitride, which is the preferred inorganic material from which solid particles useful in the present invention are formed. A non-limiting example of a useful metal oxide is zinc oxide. Suitable metal sulfides include molybdenum disulfide, tantalum disulfide, tungsten disulfide and zinc sulfide. Useful metal silicates include  
15 aluminum silicates and magnesium silicates, such as vermiculite. Suitable metallic materials include graphite, molybdenum, platinum, palladium, nickel, aluminum, copper, gold, iron, silver and mixtures thereof.

Preferably, the inorganic solid particles 24 are also solid lubricants. As used herein, "solid lubricant" means that the inorganic solid particles 24 have  
20 a characteristic crystalline habit which causes them to shear into thin, flat plates which readily slide over one another and thus produce an antifriction lubricating effect between the glass fiber surface and an adjacent solid surface, at least one of which is in motion. (See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 712, which is  
25 hereby incorporated by reference.) Friction is the resistance to sliding one solid over another. F. Clauss, Solid Lubricants and Self-Lubricating Solids, (1972) at page 1, which is hereby incorporated by reference.

In a preferred embodiment, the solid lubricant particles have a lamellar structure. Particles having a lamellar or hexagonal crystal structure are

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composed of sheets or plates of atoms in hexagonal array, with strong bonding within the sheet and weak van der Waals bonding between sheets, providing low shear strength between sheets. Friction, Wear, Lubrication at page 125, Solid Lubricants and Self-Lubricating Solids at pages 19-22, 42-54, 5 75-77, 80-81, 82, 90-102, 113-120 and 128, and W. Campbell "Solid Lubricants", Boundary Lubrication: An Appraisal of World Literature, ASME Research Committee on Lubrication (1969) at pages 202-203, which are hereby incorporated by reference. Inorganic solid particles having a lamellar fullerene (buckyball) structure are also useful in the present invention.

- 10 Non-limiting examples of suitable inorganic solid lubricant particles having a lamellar structure include boron nitride, graphite, metal dichalcogenides, mica, talc, gypsum, kaolinite, calcite, cadmium iodide, silver sulfide and mixtures thereof. Preferred inorganic solid lubricant particles include boron nitride, graphite, metal dichalcogenides and mixtures thereof.
- 15 Suitable metal dichalcogenides include molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

- Boron nitride particles having a hexagonal crystal structure are most preferred for use in the aqueous sizing composition. Boron nitride, zinc 20 sulfide and montmorillonite particles also provide good whiteness in composites with polymeric matrix materials such as nylon 6,6.

- Non-limiting examples of boron nitride particles suitable for use in the present invention are PolarTherm® 100 Series (PT 120, PT 140, PT 160 and PT 180), 300 Series (PT 350) and 600 Series (PT 620, PT 630, PT 640 and 25 PT 670) boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio. "PolarTherm® Thermally Conductive Fillers for Polymeric Materials", a technical bulletin of Advanced Ceramics Corporation of Lakewood, Ohio (1996), which is hereby incorporated by reference. These particles have a thermal conductivity of

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about 250-300 Watts per meter °K at 25°C, a dielectric constant of about 3.9 and a volume resistivity of about  $10^{15}$  ohm-centimeters. The 100 Series powder has an average particle size ranging from about 5 to about 14 micrometers, the 300 Series has an average particle size ranging from about 100 to about 150 micrometers and the 600 series has an average particle size ranging from about 16 to greater than about 200 micrometers.

The solid lubricant particles 24 can be present in a dispersion, suspension or emulsion in water. Other solvents, such as mineral oil or alcohol (preferably less than about 5 weight percent), can be included in the sizing composition, if desired. A non-limiting example of a preferred dispersion of about 25 weight percent boron nitride particles in water is ORPAC BORON NITRIDE RELEASECOAT-CONC which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee. "ORPAC BORON NITRIDE RELEASECOAT-CONC", a technical bulletin of ZYP Coatings, Inc., which is hereby incorporated by reference. According to the supplier, the boron nitride particles in this product have an average particle size of less than about 3 micrometers. This dispersion has about 1 percent of magnesium-aluminum silicate, which according to the supplier binds the boron nitride particles to the substrate to which the dispersion is applied. Other useful products which are commercially available from ZYP Coatings include BORON NITRIDE LUBRICOAT® paint, BRAZE STOP and WELD RELEASE products.

While not preferred, the coating composition can contain hydratable or hydrated inorganic solid lubricant materials. Non-limiting examples of such hydratable inorganic solid lubricant materials are clay mineral phyllosilicates, including micas (such as muscovite), talc, montmorillonite, kaolinite and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). As used herein, "hydratable" means that the solid inorganic lubricant particles react with molecules of water to form hydrates and contain water of hydration or water of crystallization. A "hydrate" is

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produced by the reaction of molecules of water with a substance in which the H-OH bond is not split. (See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 609-610 and T. Perros, Chemistry, (1967) at pages 186-187, which are hereby incorporated by reference.) In the

5 chemical formulas of hydrates, the addition of the water molecules is conventionally indicated by a centered dot, e.g.,  $3\text{MgO} \bullet 4\text{SiO}_2 \bullet \text{H}_2\text{O}$  (talca),  $\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2 \bullet 2\text{H}_2\text{O}$  (kaolinite). Hydrates contain coordinated water, which coordinates the cations in the hydrated material and cannot be removed without the breakdown of the structure, and/or structural water, which

10 occupies interstices in the structure to add to the electrostatic energy without upsetting the balance of charge. R. Evans, An Introduction to Crystal Chemistry, (1948) at page 276, which is hereby incorporated by reference.

Preferably, the coating composition is essentially free of hydratable inorganic solid lubricant particles or abrasive silica particles or calcium

15 carbonate, i.e., comprises less than about 20 weight percent of hydratable inorganic lubricant particles, abrasive silica particles or calcium carbonate on a total solids basis, more preferably less than about 5 weight percent, and most preferably less than 0.001 weight percent.

In an alternative embodiment, the solid particles 24 can be formed

20 from organic polymeric materials selected from the group consisting of thermosetting materials, thermoplastic materials, starches and mixtures thereof. Suitable thermosetting materials include thermosetting polyesters, vinyl esters, epoxy materials, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof, such as are discussed below. Suitable

25 thermoplastic materials include vinyl polymers, thermoplastic polyesters, polyolefins, polyamides, thermoplastic polyurethanes, acrylic polymers and mixtures thereof. Preferred organic solid particles are in the form of microbeads or hollow spheres.

In an alternative preferred embodiment, the solid particles 24 are thermally conductive, i.e., have a thermal conductivity greater than about 30 Watts per meter K, such as for example boron nitride, graphite, and the metallic inorganic solid lubricants discussed above. The thermal conductivity  
5 of a solid material can be determined by any method known to one skilled in the art, such as the guarded hot plate method according to ASTM C-177-85 (which is hereby incorporated by reference) at a temperature of about 300K.

In another alternative preferred embodiment, the inorganic solid particles 24 are electrically insulative or have high electrical resistivity, i.e.,  
10 have an electrical resistivity greater than about 1000 microhm-cm, such as for example boron nitride.

The solid lubricant particles, if present, can comprise about 0.001 to about 99 weight percent of the coating composition on a total solids basis, preferably, about 1 to about 80 weight percent, and more preferably about 1  
15 to about 40 weight percent.

The coating composition can further comprise one or more organic lubricants which are chemically different from the polymeric materials discussed above. While the coating composition can comprise up to about 60 weight percent organic lubricants, preferably the coating composition is  
20 essentially free of organic lubricants, i.e., contains less than about 10 weight percent of organic lubricants, and more preferably contains about 1 to about 5 weight percent of organic lubricants. Examples of such organic lubricants include cationic, non-ionic or anionic lubricants and mixtures thereof, such as amine salts of fatty acids, alkyl imidazoline derivatives such as CATION X,  
25 which is commercially available from Rhone Poulenc of Princeton, New Jersey, acid solubilized fatty acid amides, condensates of a fatty acid and polyethylene imine and amide substituted polyethylene imines, such as EMERY® 6717, a partially amidated polyethylene imine commercially available from Henkel Corporation of Kankakee, Illinois.

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The coating composition can include one or more emulsifying agents for emulsifying or dispersing components of the coating composition, such as the inorganic particles. Non-limiting examples of suitable emulsifying agents or surfactants include polyoxyalkylene block copolymers (such as PLURONIC<sup>™</sup> F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey), ethoxylated alkyl phenols (such as IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey), polyoxyethylene octylphenyl glycol ethers, ethylene oxide derivatives of sorbitol esters, polyoxyethylated vegetable oils (such as ALKAMULS EL-719, which is commercially available from Rhone-Poulenc) and nonylphenol surfactants (such as MACOL NP-6 which is commercially available from BASF of Parsippany, New Jersey). Generally, the amount of emulsifying agent can range from about 1 to about 30 weight percent of the coating composition on a total solids basis.

The coating composition can include one or more aqueous soluble, emulsifiable or dispersible wax materials such as vegetable, animal, mineral, synthetic or petroleum waxes. Preferred waxes are petroleum waxes such as MICHEM® LUBE 296 microcrystalline wax, POLYMEKON® SPP-W microcrystalline wax and PETROLITE 75 microcrystalline wax which are commercially available from Michelman Inc. of Cincinnati, Ohio and the Petrolite Corporation of Tulsa, Oklahoma, respectively. Generally, the amount of wax can be about 1 to about 10 weight percent of the coating on a total solids basis.

Crosslinking materials, such as melamine formaldehyde, and plasticizers, such as phthalates, trimellitates and adipates, can also be included in the coating composition. The amount of crosslinker or plasticizer can range from about 1 to about 5 weight percent of the coating composition on a total solids basis.

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Other additives can be included in the coating composition, such as silicones, fungicides, bactericides and anti-foaming materials, generally in an amount of less than about 5 weight percent. Organic and/or inorganic acids or bases in an amount sufficient to provide the coating composition with a pH of about 2 to about 10 can also be included. A non-limiting example of a suitable silicone emulsion is LE-9300 epoxidized silicone emulsion which is commercially available from OSi Specialties, Inc. of Danbury, Connecticut. An example of a suitable bactericide is Biomet 66 antimicrobial compound, which is commercially available from M & T Chemicals of Rahway, New Jersey. Suitable anti-foaming materials are the SAG materials, which are commercially available from OSi Specialties, Inc. of Danbury, Connecticut and MAZU DF-136, which is available from BASF Company of Parsippany, New Jersey. Ammonium hydroxide can be added to the coating composition for stabilization, if desired. Water (preferably deionized) is preferably included in the coating composition in an amount sufficient to facilitate application of a generally uniform coating upon the strand, generally in an amount of about 25 to about 99 weight percent. The weight percentage of solids of an aqueous coating composition generally ranges from about 1 to about 75 weight percent.

The coating composition is preferably essentially free of glass materials. As used herein, "essentially free of glass materials" means that the coating composition comprises less than 20 volume percent of glass matrix materials for forming glass composites, preferably less than about 5 volume percent, and more preferably is free of glass materials. Examples of such glass matrix materials include black glass ceramic matrix materials or aluminosilicate matrix materials such as are well known to those skilled in the art.

In one embodiment for weaving fabric for printed circuit boards, the glass fibers of the coated fiber strands of the present invention have applied

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thereto a primary layer of a dried residue of an aqueous sizing composition comprising PolarTherm® 160 boron nitride powder and/or BORON NITRIDE RELEASECOAT dispersion, EPON 826 epoxy film-forming material, PVP K-30 polyvinyl pyrrolidone, A-187 epoxy-functional organo silane coupling agent, ALKAMULS EL-719 polyoxyethylated vegetable oil, IGEPAL CA-630 ethoxylated octylphenoxyethanol, KESSCO PEG 600 polyethylene glycol monolaurate ester which is commercially available from Stepan Company of Chicago, Illinois and EMERY® 6717 partially amidated polyethylene imine.

In a preferred embodiment for weaving cloth, glass fibers of the coated fiber strands of the present invention have applied thereto a primary layer of a dried residue of an aqueous sizing composition comprising PolarTherm® 160 boron nitride powder and/or BORON NITRIDE RELEASECOAT dispersion, RD-847A polyester, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester, A-174 acrylic-functional organo silane coupling agent and A-187 epoxy-functional organo silane coupling agent.

The coating compositions of the present invention can be prepared by any suitable method such as conventional mixing well known to those skilled in the art. Preferably, the components discussed above are diluted with water to have the desired weight percent solids and mixed together. Powdered thermally conductive inorganic solid particles can be premixed with water or added to the polymeric material prior to mixing with the other components of the coating.

The layer of coating can be applied to the fibers in many ways, for example by contacting the filaments with a roller or belt applicator, spraying or other means. The coated fibers are preferably dried at room temperature or at elevated temperatures. The dryer removes excess moisture from the fibers and, if present, cures any curable coating composition components. The temperature and time for drying the glass fibers will depend upon such variables as the percentage of solids in the coating composition, components



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of the coating composition and type of glass fiber. The coating composition is typically present as a dried sizing residue on the fibers in an amount between about 0.1 percent and about 25 percent by weight after drying. The loss on ignition of the fibers is generally less than about 0.6 weight percent,

- 5 preferably less than about 0.5 weight percent, and more preferably ranges from about 0.01 to about 0.45 weight percent. The loss on ignition of a sample of coated fiber can be determined by heating the fiber for 20 minutes in a muffle furnace at a temperature of 1200°C.

- A secondary layer of a secondary coating composition can be applied  
10 over the layer of coating composition discussed above in an amount effective to coat or impregnate the portion of the strands, for example by dipping the strand in a bath containing the composition, spraying the composition upon the strand or by contacting the strand with an applicator as discussed above. The coated strand can be passed through a die to remove excess coating  
15 composition from the strand and/or dried as discussed above for a time sufficient to at least partially dry or cure the secondary coating composition. The method and apparatus for applying the secondary coating composition to the strand is determined in part by the configuration of the strand material. The strand is preferably dried after application of the secondary coating  
20 composition in a manner well known in the art.

- Suitable secondary coating compositions can include one or more film-forming materials, lubricants and other additives such as are discussed above. The secondary coating is different from the sizing composition, i.e., it  
(1) contains at least one component which is chemically different from the  
25 components of the sizing composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the sizing composition. Non-limiting examples of suitable secondary coating compositions including polyurethane are disclosed in U.S.

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Patent Nos. 4,762,750 and 4,762,751, which are hereby incorporated by reference.

- In an alternative preferred embodiment according to the present invention, the glass fibers of the fiber strand can having applied thereto a
- 5 primary layer of a dried residue of a conventional sizing composition or a sizing composition which can include any of the sizing components in the amounts discussed above. Examples of suitable sizing compositions are set forth in Loewenstein at pages 237-291 (3d Ed. 1993) and U.S. Patent Nos. 4,390,647 and 4,795,678, each of which is hereby incorporated by reference.
- 10 A secondary or principal layer of a secondary coating composition according to the present invention is applied to at least a portion, and preferably over the entire outer surface, of the primary layer. The secondary coating composition can comprise one or more types of solid particles discussed above and/or those which are set forth in Tables C, D and E below.

15

**Table C**

Inorganic Solid Material	Thermal conductivity (W/m K at 300K)	Electrical Resistance (micro ohm-centimeters)	Mohs' hardness (original scale)
boron nitride	about 200 <sup>19</sup>	$1.7 \times 10^{19-20}$	about 2 <sup>21</sup>
boron phosphide	about 350 <sup>22</sup>	-	about 9.5 <sup>23</sup>
aluminum phosphide	about 130 <sup>24</sup>	-	-
aluminum nitride	about 200 <sup>25</sup>	greater than $10^{19-26}$	about 9 <sup>27</sup>
gallium nitride	about 170 <sup>28</sup>	-	-
gallium phosphide	about 100 <sup>29</sup>	-	-
silicon carbide	about 270 <sup>30</sup>	$4 \times 10^5$ to $1 \times 10^{6-31}$	greater than 9 <sup>32</sup>
silicon nitride	about 30 <sup>33</sup>	$10^{19}$ to $10^{20-34}$	about 9 <sup>35</sup>
beryllium oxide	about 240 <sup>36</sup>	-	about 9 <sup>37</sup>

19 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 322, which is hereby incorporated by reference.

20 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 654.

21 Friction, Wear, Lubrication at page 27.

22 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 325, which is hereby incorporated by reference.

23 R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 164, which is hereby incorporated by reference.

24 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 333, which is hereby incorporated by reference.

25 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 329, which is hereby incorporated by reference.

26 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 654.

27 Friction, Wear, Lubrication at page 27.

28 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 333.

29 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 321, which is hereby incorporated by reference.

30 Microelectronics Packaging Handbook at page 36, which is hereby incorporated by reference.

31 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 653, which is hereby incorporated by reference.

32 Friction, Wear, Lubrication at page 27.

33 Microelectronics Packaging Handbook at page 36, which is hereby incorporated by reference.

34 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 654.

35 Friction, Wear, Lubrication at page 27.

36 Microelectronics Packaging Handbook at page 905, which is hereby incorporated by reference.

37 Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 141, which is hereby incorporated by reference.

**Table D**

Inorganic Solid Material	Thermal conductivity (W/m K at 300K)	Electrical Resistance (micro ohm-centimeters)	Mohs' hardness (original scale)
zinc oxide	about 26	-	about 4.5 <sup>38</sup>
zinc sulfide	about 25 <sup>39</sup>	$2.7 \times 10^5$ to $1.2 \times 10^{12}$ <sup>40</sup>	about 3.5-4 <sup>41</sup>
diamond	about 2300 <sup>42</sup>	$2.7 \times 10^8$ <sup>43</sup>	10 <sup>44</sup>
silicon	about 84 <sup>45</sup>	about 10.0 <sup>46</sup>	about 7 <sup>47</sup>
graphite	up to 2000 <sup>48</sup>	100 <sup>49</sup>	about 0.5-1 <sup>50</sup>
molybdenum	about 138 <sup>51</sup>	about 5.2 <sup>52</sup>	
platinum	about 69 <sup>53</sup>	about 10.6 <sup>54</sup>	about 4.3 <sup>55</sup>
palladium	about 70 <sup>56</sup>	about 10.8 <sup>57</sup>	about 4.8 <sup>58</sup>
tungsten	about 200 <sup>59</sup>	about 5.5 <sup>60</sup>	
nickel	about 92 <sup>61</sup>	about 6.8 <sup>62</sup>	about 5 <sup>63</sup>
aluminum	about 205 <sup>64</sup>	about 4.3 <sup>65</sup>	about 2.5 <sup>66</sup>
chromium	about 66 <sup>67</sup>	about 20 <sup>68</sup>	about 9.0 <sup>69</sup>

38 Friction, Wear, Lubrication at page 27.

39 Handbook of Chemistry and Physics, CRC Press (1975) at page 12-54.

40 Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 12-63, which is hereby incorporated by reference.

41 Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 4-158, which is hereby incorporated by reference.

42 Microelectronics Packaging Handbook at page 36.

43 Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 12-63, which is hereby incorporated by reference.

44 Handbook of Chemistry and Physics at page F-22.

45 Microelectronics Packaging Handbook at page 174.

46 Handbook of Chemistry and Physics at page F-166, which is hereby incorporated by reference.

47 Friction, Wear, Lubrication at page 27.

48 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 322, which is hereby incorporated by reference.

49 See W. Callister, Materials Science and Engineering An Introduction, (2d ed. 1991) at page 637, which is hereby incorporated by reference.

50 Handbook of Chemistry and Physics at page F-22.

51 Microelectronics Packaging Handbook at page 174.

52 Microelectronics Packaging Handbook at page 37.

53 Microelectronics Packaging Handbook at page 174.

54 Microelectronics Packaging Handbook at page 37.

55 Handbook of Chemistry and Physics at page F-22.

56 Microelectronics Packaging Handbook at page 37.

57 Microelectronics Packaging Handbook at page 37.

58 Handbook of Chemistry and Physics at page F-22.

59 Microelectronics Packaging Handbook at page 37.

60 Microelectronics Packaging Handbook at page 37.

61 Microelectronics Packaging Handbook at page 174.

62 Microelectronics Packaging Handbook at page 37.

63 Handbook of Chemistry and Physics at page F-22.

64 Microelectronics Packaging Handbook at page 174.

65 Microelectronics Packaging Handbook at page 37.

66 Friction, Wear, Lubrication at page 27.

67 Microelectronics Packaging Handbook at page 37.

68 Microelectronics Packaging Handbook at page 37.

69 Handbook of Chemistry and Physics at page F-22.

**Table E**

Inorganic Solid Material	Thermal conductivity (W/m K at 300K)	Electrical Resistance (micro ohm- centimeters)	Mohs' hardness (original scale)
copper	about 398 <sup>70</sup>	about 1.7 <sup>71</sup>	about 2.5-3 <sup>72</sup>
gold	about 297 <sup>73</sup>	about 2.2 <sup>74</sup>	about 2.5-3 <sup>75</sup>
iron	about 74.5 <sup>76</sup>	about 9 <sup>77</sup>	about 4-5 <sup>78</sup>
silver	about 418 <sup>79</sup>	about 1.6 <sup>80</sup>	about 2.5-4 <sup>81</sup>

Molybdenum disulfide and magnesium oxide are other inorganic solid  
 5 particles which are useful for secondary or tertiary coatings of the present  
 invention. One skilled in the art would understand that mixtures of any of the  
 above inorganic solid particles can be used in the present invention.

The amount of inorganic particles in the secondary coating  
 composition can range from about 1 to about 99 weight percent on a total  
 10 solids basis, and preferably about 20 to about 90 weight percent. The  
 percentage of solids of an aqueous secondary coating composition generally  
 ranges from about 5 to about 75 weight percent.

In an alternative embodiment, a tertiary layer of a tertiary coating  
 composition can be applied over at least a portion of the surface, and  
 15 preferably over the entire surface, of a secondary layer, i.e., such a fiber  
 strand would have a primary layer of sizing, a secondary layer of a secondary  
 coating composition and a tertiary, outer layer of the tertiary coating. The  
 tertiary coating is different from the sizing composition and the secondary

<sup>70</sup> Microelectronics Packaging Handbook at page 174.

<sup>71</sup> Microelectronics Packaging Handbook at page 37.

<sup>72</sup> Handbook of Chemistry and Physics, at page F-22.

<sup>73</sup> Microelectronics Packaging Handbook at page 174.

<sup>74</sup> Microelectronics Packaging Handbook at page 37.

<sup>75</sup> Handbook of Chemistry and Physics at page F-22.

<sup>76</sup> Microelectronics Packaging Handbook at page 174.

<sup>77</sup> Handbook of Chemistry and Physics, CRC Press (1975) at page D-171, which is hereby  
 incorporated by reference.

<sup>78</sup> Handbook of Chemistry and Physics at page F-22.

<sup>79</sup> Microelectronics Packaging Handbook at page 174.

<sup>80</sup> Microelectronics Packaging Handbook at page 37.

<sup>81</sup> Handbook of Chemistry and Physics at page F-22.

coating composition, i.e., the tertiary coating composition (1) contains at least one component which is chemically different from the components of the sizing and secondary coating composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the sizing or secondary coating composition.

In this embodiment, the secondary coating composition comprises one or more polymeric materials discussed above, such as polyurethane, and the tertiary coating composition comprises powdered thermally conductive inorganic particles, such as the PolarTherm® boron nitride particles which are discussed above. Preferably, the powdered coating is applied by passing the strand having a liquid secondary coating composition applied thereto through a fluidized bed or spray device to adhere the powder particles to the tacky secondary coating composition. Alternatively, the strands can be assembled into a fabric 114 before the layer 140 of tertiary coating is applied, as shown in Fig. 5. The weight percent of powdered, thermally conductive inorganic solid particles adhered to the coated strand can range from about 0.1 to about 75 weight percent of the total weight of the dried strand. The tertiary coating can also include one or more polymeric materials such as are discussed above, such as acrylic polymers, epoxies, or polyolefins, conventional stabilizers and other modifiers known in the art of such coatings, preferably in dry powdered form.

The fiber strands can be processed into a woven fabric 14, preferably by knitting or weaving. The woven fabric 14 is used as a reinforcement for reinforcing polymeric matrix materials 12 to form a composite or laminate 10, such as is shown in Fig. 1, preferably for use in printed circuit boards. The warp strands of fabric 14 can be untwisted or twisted prior to weaving by any conventional twisting technique known to those skilled in the art, for example by using twist frames to impart twist to the strand at about 0.5 to about 3 turns per inch.

The reinforcing fabric 14 can include about 5 to about 100 warp strands per centimeter and preferably has about 3 to about 25 picks per centimeter (about 1 to about 15 picks per inch) of the weft strand. The weave construction can be a regular plain weave, although any other weaving style well known to those skilled in the art, such as a twill weave or satin weave, can be used.

The fabric 14 is preferably woven in a style which is suitable for use in a laminate for printed circuit boards, such as are disclosed in "Fabrics Around the World", a technical bulletin of Clark-Schwebel, Inc. of Anderson, South Carolina (1995), which is hereby incorporated by reference. A preferred fabric style using E225 E-glass fibers is Style 2116, which has 118 warp yarns and 114 weft yarns per 5 centimeter square area (60 warp yarns and 58 weft yarns per square inch); uses 7 22 1x0 (E225 1/0) warp and weft yarn; has a nominal fabric thickness of 0.094 mm ( 0.037 inches); and a fabric weight of 103.8 g/m<sup>2</sup> (3.06 ounces per square yard). A preferred fabric style using G75 E-glass fibers is Style 7628, which has 87 warp yarns and 61 weft yarns per 5 centimeter square area (44 warp yarns and 31 weft yarns per square inch); uses 9 68 1x0 (G75 1/0) warp and weft yarn; has a nominal fabric thickness of 0.173 mm ( 0.0068 inches); and a fabric weight of 203.4 g/m<sup>2</sup> (6.00 ounces per square yard). A preferred fabric style using D450 E-glass fibers is Style 1080, which has 118 warp yarns and 93 weft yarns per 5 centimeter square area (60 warp yarns and 47 weft yarns per square inch); uses 5 11 1x0 (D450 1/0) warp and weft yarn; has a nominal fabric thickness of 0.053 mm ( 0.0021 inches); and a fabric weight of 46.8 g/m<sup>2</sup> (1.38 ounces per square yard). These and other useful fabric style specifications are given in IPC-EG-140 "Specification for Finished Fabric Woven from 'E' Glass for Printed Boards", a publication of The Institute for Interconnecting and Packaging Electronic Circuits (June 1997), which is hereby incorporated by reference.

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A suitable woven reinforcing fabric 14 can be formed by using any conventional loom well known to those skilled in the art, such as a shuttle loom or rapier loom, but preferably is formed using an air jet loom. Preferred air jet looms are commercially available from Tsudakoma of Japan as Model  
5 No. 103 and Sulzer Ruti Model No. L-5000 or L-5100, which are commercially available from Sulzer Brothers Ltd. of Zurich, Switzerland. Sulzer Ruti L5000 and L5100 Product Bulletins of Sulzer Ruti Ltd., Switzerland, which are hereby incorporated by reference.

As used herein, "air jet weaving" means a type of fabric weaving using  
10 an air jet loom 526 (shown in Fig. 6) in which the fill yarn (weft) 510 is inserted into the warp shed by a blast of compressed air 514 from one or more air jet nozzles 518 (shown in Figs. 6 and 6a), as discussed above. The fill yarn 510 is propelled across the width 524 of the fabric 528 (about 10 to about 60 inches), and more preferably about 0.91 meters (about 36 inches) by the  
15 compressed air.

The air jet filling system can have a single, main nozzle 516, but preferably also has a plurality of supplementary, relay nozzles 520 along the warp shed 512 for providing blasts of supplementary air 522 to the fill yarn 510 to maintain the desired air pressure as the yarn 510 traverses the width  
20 524 of the fabric 528. The air pressure (gauge) supplied to the main air nozzle 516 preferably ranges from about 103 to about 413 kiloPascals (kPa) (about 15 to about 60 pounds per square inch (psi)), and more preferably is about 310 kPa (about 45 psi). The preferred style of main air nozzle 516 is a Sulzer Ruti needle air jet nozzle unit Model No. 044 455 001 which has an  
25 internal air jet chamber having a diameter 517 of 2 millimeters and a nozzle exit tube 519 having a length 521 of 20 centimeters (commercially available from Sulzer Ruti of Spartanburg, North Carolina). Preferably, the air jet filling system has 15 to about 20 supplementary air nozzles 520 which supply auxiliary blasts of air in the direction of travel of the fill yarn 510 to assist in



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propelling the yarn 510 across the loom 526. The air pressure (gauge) supplied to each supplementary air nozzle 520 preferably ranges from about 3 to about 6 bars.

The fill yarn 510 is drawn from the supply package 530 by a feeding  
5 system 532 at a feed rate of about 180 to about 550 meters per minute, and preferably about 274 meters (about 300 yards) per minute. The fill yarn 510 is fed into the main nozzle 518 through a clamp. A blast of air propels a predetermined length of yarn (approximately equal to the desired width of the fabric) through the confusor guide. When the insertion is completed, the end  
10 of the yarn distal to the main nozzle 518 is cut by a cutter 534.

The compatibility and aerodynamic properties of different yarns with the air jet weaving process can be determined by the following method, which will generally be referred to herein as the "Air Jet Transport Drag Force" Test Method. The Air Jet Transport Drag Force Test is used to measure the  
15 attractive or pulling force ("drag force") exerted upon the yarn as the yarn is pulled into the air jet nozzle by the force of the air jet. In this method, each yarn sample is fed at a rate of about 274 meters (about 300 yards) per minute through a Sulzer Ruti needle air jet nozzle unit Model No. 044 455 001 which has an internal air jet chamber having a diameter 517 of 2 millimeters and a  
20 nozzle exit tube 519 having a length 521 of 20 centimeters (commercially available from Sulzer Ruti of Spartanburg, North Carolina) at an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge. A tensiometer is positioned in contact with the yarn at a position prior to the yarn entering the air jet nozzle. The tensiometer provides a measurement of  
25 the gram force (drag force) exerted upon the yarn by the air jet as the yarn is pulled into the air jet nozzle.

The drag force per unit mass can be used as a basis for relative comparison of yarn samples. For relative comparison, the drag force measurements are normalized over a one centimeter length of yarn. The

Gram Mass of a one centimeter length of yarn can be determined according to formula (I):

$$\text{Gram Mass} = (\pi (d/2)^2) (N) (\rho_{\text{glass}}) (1 \text{ centimeter length of yarn}) \quad (I)$$

where d is the diameter of a single fiber of the yarn bundle, N is the number of  
 5 fibers in the yarn bundle and  $\rho_{\text{glass}}$  is the density of the glass at a temperature of about 25°C (about 2.6 grams per cubic centimeter). Table F lists the diameters and number of fibers in a yarn for several typical glass fiber yarn products.

10

**Table F**

Yarn type	Fiber Diameter (centimeters)	Number of Fibers in Bundle
G75	$9 \times 10^{-4}$	400
G150	$9 \times 10^{-4}$	200
E225	$7 \times 10^{-4}$	200
D450	$5.72 \times 10^{-4}$	200

For example, the Gram Mass of a one centimeter length of G75 yarn is  $(\pi (9 \times 10^{-4}/2)^2) (400) (2.6 \text{ grams per cubic centimeter}) (1 \text{ centimeter length of yarn}) = 6.62 \times 10^{-4}$  gram mass. For D450 yarn, the Gram Mass is  $1.34 \times 10^{-4}$   
 15 gram mass. The relative drag force per unit mass ("Air Jet Transport Drag Force") is calculated by dividing the drag force measurement (gram force) determined by the tensiometer by the Gram Mass for the type of yarn tested. For example, for a sample of G75 yarn, if the tensiometer measurement of the drag force is 68.5, then the Air Jet Transport Drag Force is equal to 68.5  
 20 divided by  $6.62 \times 10^{-4} = 103,474$  gram force per gram mass of yarn.

The Air Jet Transport Drag Force of the yarn used to form a woven fabric for a laminate according to the present invention, determined according to the Air Jet Transport Drag Force Test Method discussed above, is greater than about 100,000 gram force per gram mass of yarn, preferably ranges  
 25 from about 100,000 to about 400,000 gram force per gram mass of yarn, and

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more preferably ranges from about 120,000 to about 300,000 gram force per gram mass of yarn.

Referring now to Fig. 1, the fabric 14 can be used to form a laminate 10 by coating and/or impregnating one or more layers of the fabric 14 with a polymeric thermoplastic or thermosetting matrix material 12. The laminate 10 is suitable for use as an electronic support 30. As used herein, "electronic support" means a structure that mechanically supports and/or electrically interconnects elements including but not limited to active electronic components, passive electronic components, printed circuits, integrated circuits, semiconductor devices and other hardware associated with such elements including but not limited to connectors, sockets, retaining clips and heat sinks.

Matrix materials useful in the present invention include thermosetting materials such as thermosetting polyesters, vinyl esters, epoxides (containing at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols), phenolics, aminoplasts, thermosetting polyurethanes, derivatives and mixtures thereof. Preferred matrix materials for forming laminates for printed circuit boards are FR-4 epoxy resins, polyimides and liquid crystalline polymers, the compositions of which are well known to those skilled in the art. If further information regarding such compositions is needed, see 1 Electronic Materials Handbook™, ASM International (1989) at pages 534-537.

Non-limiting examples of suitable thermoplastic polymeric matrix materials include polyolefins, polyamides, thermoplastic polyurethanes and thermoplastic polyesters, vinyl polymers and mixtures thereof. Further examples of useful thermoplastic materials include polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polyvinyl chlorides and polycarbonates.

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A useful matrix material formulation consists of EPON 1120-A80 epoxy resin, dicyandiamide, 2-methylimidazole and DOWANOL PM.

Other components which can be included with the polymeric matrix material and reinforcing material in the composite include colorants or pigments, lubricants or processing aids, ultraviolet light (UV) stabilizers, antioxidants, other fillers and extenders.

The fabric 14 can be coated and impregnated by dipping the fabric 14 in a bath of the polymeric matrix material 12, for example, as discussed in R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 895-896, which are hereby incorporated by reference. The polymeric matrix material 12 and fabric 14 can be formed into a composite or laminate 10 by a variety of methods which are dependent upon such factors as the type of polymeric matrix material used. For example, for a thermosetting matrix material, the laminate can be formed by compression or injection molding, pultrusion, hand lay-up, or by sheet molding followed by compression or injection molding. Thermosetting polymeric matrix materials can be cured by the inclusion of crosslinkers in the matrix material and/or by the application of heat, for example. Suitable crosslinkers useful to crosslink the polymeric matrix material are discussed above. The temperature and curing time for the thermosetting polymeric matrix material depends upon such factors as the type of polymeric matrix material used, other additives in the matrix system and thickness of the composite, to name a few.

For a thermoplastic matrix material, suitable methods for forming the composite include direct molding or extrusion compounding followed by injection molding. Methods and apparatus for forming the composite by the above methods are discussed in I. Rubin, Handbook of Plastic Materials and Technology (1990) at pages 955-1062, 1179-1215 and 1225-1271, which are hereby incorporated by reference.

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In a particular embodiment of the invention shown in Fig. 4, composite or laminate 10 includes fabric 14 impregnated with a compatible matrix material 12. The impregnated fabric can then be squeezed between a set of metering rolls to leave a measured amount of matrix material, and dried to  
5 form an electronic support in the form of a semicured substrate or prepreg. An electrically conductive layer 40 can be positioned along a portion of a side 42 of the prepreg in a manner to be discussed below in the specification, and the prepreg is cured to form a laminate 10 which functions as an electronic support 50 with an electrically conductive layer. In another embodiment of  
10 the invention, and more typically in the electronic support industry, two or more prepreps are combined with an electrically conductive layer and laminated together and cured in a manner well known to those skilled in the art, to form a multilayered electronic support. For example, but not limiting the present invention, the prepreg stack can be laminated by pressing the  
15 stack, e.g. between polished steel plates, at elevated temperatures and pressures for a predetermined length of time to cure the polymeric matrix and form a laminate of a desired thickness. A portion of one or more of the prepreps can be provided with an electrically conductive layer either prior to or after lamination and curing such that the resulting electronic support is a  
20 laminate having at least one electrically conductive layer along a portion of an exposed surface (hereinafter referred to as a "clad laminate").

Circuits can then be formed from the electrically conductive layer(s) of the single layer or multilayered electronic support using techniques well known in the art to construct an electronic support in the form of a printed  
25 circuit board or printed wiring board (hereinafter collectively referred to as "electronic circuit boards"). If desired, apertures or holes (also referred to as "vias") can be formed in the electronic supports, to allow for electrical interconnection between circuits and/or components on opposing surfaces of the electronic support, by any convenient manner known in the art, including

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but not limited to mechanical drilling and laser drilling. More specifically, after formation of the apertures, a layer of electrically conductive material is deposited on the walls of the aperture or the aperture is filled with an electrically conductive material to facilitate the required electrical

5 interconnection and/or heat dissipation.

The electrically conductive layer 40 can be formed by any method well known to those skilled in the art. For example but not limiting the present invention, the electrically conductive layer can be formed by laminating a thin sheet or foil of metallic material onto at least a portion of a side of the semi-  
10 cured or cured prepreg or laminate. As an alternative, the electrically conductive layer can be formed by depositing a layer of metallic material onto at least a portion of a side of the semi-cured or cured prepreg or laminate using well known techniques including but not limited to electrolytic plating, electroless plating or sputtering. Metallic materials suitable for use as an  
15 electrically conductive layer include but are not limited to copper (which is preferred), silver, aluminum, gold, tin, tin-lead alloys, palladium and combinations thereof.

In another embodiment of the present invention, the electronic support can be in the form of a multilayered electronic circuit board constructed by  
20 laminating together one or more electronic circuit boards (described above) with one or more clad laminates (described above) and/or one or more prepreps (described above). If desired, additional electrically conductive layers can be incorporated into the electronic support, for example along a portion of an exposed side of the multilayered electronic circuit board.  
25 Furthermore, if required, additional circuits can be formed from the electrically conductive layers in a manner discussed above. It should be appreciated that depending on the relative positions of the layers of the multilayered electronic circuit board, the board can have both internal and external circuits. Additional apertures are formed, as discussed earlier, partially through or

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completely through the board to allow electrical interconnection between the layers at selected locations. It should be appreciated that the resulting structure can have some apertures that extend completely through the structure, some apertures that extend only partially through the structure, and  
5 some apertures that are completely within the structure.

Preferably, the thickness of the laminate forming the electronic support  
50 is greater than about 0.051 mm (0.002 inches), and more preferably ranges from about 0.13 mm (0.005 inches) to about 2.5 mm (about 0.1 inches). For an eight ply laminate of 7628 style fabric, the thickness is  
10 generally about 1.32 mm (0.052 inches). The number of layers of fabric 14 in the laminate 10 can vary based upon the desired thickness of the laminate. For clarity in the drawings, only a single layer of fabric is shown in the laminates of Figs. 1, 4 and 5. The number of layers can range from one to about 40. Preferably, the laminate has eight layers of fabric or prepreg.

15 The resin content of the laminate can range from about 35 to about 80 weight percent, and more preferably about 40 to about 75 weight percent. The amount of fabric in the laminate can range from about 20 to about 65 weight percent and more preferably ranges from about 25 to about 60 weight percent.

20 For a laminate formed from woven E-glass fabric and using an FR-4 epoxy resin matrix material having a minimum glass transition temperature of about 110°C, the desired minimum flexural strength in the cross machine or width direction (generally perpendicular to the longitudinal axis of the fabric) is greater than  $3 \times 10^7$  kg/m<sup>2</sup>, preferably greater than about  $3.52 \times 10^7$  kg/m<sup>2</sup>  
25 (about 50 kpsi), and more preferably greater than about  $4.9 \times 10^7$  kg/m<sup>2</sup> (about 70 kpsi) according to IPC-4101 "Specification for Base Materials for Rigid and Multilayer Printed Boards" at page 29, a publication of The Institute for Interconnecting and Packaging Electronic Circuits (December 1997). IPC-4101 is hereby incorporated by reference in its entirety. In the length

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direction, the desired minimum flexural strength in the length direction (generally parallel to the longitudinal axis of the fabric) is greater than about  $4 \times 10^7$  kg/m<sup>2</sup>, and preferably greater than  $4.23 \times 10^7$  kg/m<sup>2</sup>. The flexural strength is measured according to ASTM D-790 and IPC-TM-650 Test

- 5 Methods Manual of the Institute for Interconnecting and Packaging Electronics (December 1994) (which are hereby incorporated by reference) with metal cladding completely removed by etching according to section 3.8.2.4 of IPC-4101. Advantages of the electronic supports of the present invention include high flexural strength (tensile and compressive strength)
- 10 and high modulus, which can lessen deformation of a circuit board including the laminate.

- Electronic supports of the present invention in the form of copper clad FR-4 epoxy laminates preferably have a coefficient of thermal expansion at 288°C in the z-direction of the laminate ("Z-CTE"), i.e., across the thickness of
- 15 the laminate, of less than about 4.5 percent, and more preferably ranging from about 0.01 to about 4.5 weight percent, according to IPC Test Method 2.4.41 (which is hereby incorporated by reference). Each such laminate preferably contains eight layers of 7628 style fabric, although styles 1080 or 2116 style fabrics can alternatively be used. Laminates having low
- 20 coefficients of thermal expansion are generally less susceptible to expansion and contraction and can minimize board distortion.

- The instant invention further contemplates the fabrication of multilayered laminates and electronic circuit boards which include at least one composite layer made according to the teachings herein and at least one
- 25 composite layer made in a manner different from the composite layer taught herein, e.g. made using conventional glass fiber composite technology. More specifically and as is well known to those skilled in the art, traditionally the filaments in continuous glass fiber strands used in weaving fabric are treated with a starch/oil sizing which includes partially or fully dextrinized starch or



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amylose, hydrogenated vegetable oil, a cationic wetting agent, emulsifying agent and water, including but not limited to those disclosed in Lowenstein at pages 237-244 (3d Ed. 1993), which is hereby incorporated by reference.

Warp yarns produced from these strands are thereafter treated with a solution  
5 prior to weaving to protect the strands against abrasion during the weaving process, e.g. poly(vinyl alcohol) as disclosed in U.S. Patent No. 4,530,876 at column 3, line 67 through column 4, line 11, which is hereby incorporated by reference. This operation is commonly referred to as slashing. The poly(vinyl alcohol) as well as the starch/oil size are generally not compatible with the  
10 polymeric matrix material used by composite manufacturers and the fabric must be cleaned to remove essentially all organic material from the surface of the glass fibers prior to impregnating the woven fabric. This can be accomplished in a variety ways, for example by scrubbing the fabric or, more commonly, by heat treating the fabric in a manner well known in the art. As a  
15 result of the cleaning operation, there is no suitable interface between the polymeric matrix material used to impregnate the fabric and the cleaned glass fiber surface, so that a coupling agent must be applied to the glass fiber surface. This operation is sometime referred to by those skilled in the art as finishing. The coupling agents most commonly used in finishing operations  
20 are silanes, including but not limited to those disclosed in E. P. Plueddemann, Silane Coupling Agents (1982) at pages 146-147, which is hereby incorporated by reference. Also see Lowenstein at pages 249-256 (3d Ed. 1993). After treatment with the silane, the fabric is impregnated with a compatible polymeric matrix material, squeezed between a set of metering  
25 rolls and dried to form a semicured prepreg as discussed above. It should be appreciated that depending on the nature of the sizing, the cleaning operation and/or the matrix resin used in the composite, the slashing and/or finishing steps can be eliminated. One or more prepregs incorporating conventional glass fiber composite technology can then be combined with one or more

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prepregs incorporating the instant invention to form an electronic support as discussed above, and in particular a multilayered laminate or electronic circuit board. For more information regarding fabrication of electronic circuit boards, see 1 Electronic Materials Handbook<sup>TM</sup>, ASM International (1989) at pages  
5 113-115, R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 858-861 and 895-909, M. W. Jawitz, Printed Circuit Board Handbook (1997) at pages 9.1-9.42, and C. F. Coombs, Jr. (Ed.), Printed Circuits Handbook, (3d Ed. 1988), pages 6.1-6.7, which are hereby incorporated by reference.

10 The composites and laminates forming the electronic supports of the instant invention can be used to form packaging used in the electronics industry, and more particularly first, second and/or third level packaging, such as that disclosed in Tummala at pages 25-43, which is hereby incorporated by reference. In addition, the present invention can also be used for other  
15 packaging levels.

The present invention also includes a method for assembling a fabric  
14 by interweaving a first yarn (weft) with a second yarn (warp) to form the fabric 14, for example by air jet weaving as discussed above. The improvement comprises the first yarn comprising E-glass fibers having a coating  
20 which is compatible with a polymeric matrix material, the coating comprising (1) one or more polyesters and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers, starches and mixtures thereof (which are discussed in detail above).

Another aspect of the present invention is a method for forming a  
25 laminate of a woven fabric and a polymeric matrix material by coating the woven fabric with the polymeric matrix material to form a coated fabric and applying heat to the coated fabric. The woven fabric comprises a yarn comprising E-glass fibers. The improvement comprises the E-glass fibers having a coating which is compatible with the polymeric matrix material, the

yarn having an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit as described in detail above at a feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, and the laminate having a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi).

Another aspect of the present invention is a method for forming a laminate of a woven fabric and a polymeric matrix material by coating the woven fabric with the polymeric matrix material to form a coated fabric and applying heat to the coated fabric. The woven fabric comprising a yarn comprising E-glass fibers. The improvement comprises the E-glass fibers having a coating which is compatible with a polymeric matrix material, the coating comprising: (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches.

The present invention will now be illustrated by the following specific, non-limiting examples.

20

### EXAMPLE 1

The compatibility of samples of several different yarns with the air jet weaving process were determined using the "Air Jet Transport Drag Force" Test Method discussed in detail above.

Yarn samples according to the present invention were coated with matrix resin-compatible aqueous forming size compositions A-F according to Table 1A below and evaluated using the "Air Jet Transport Drag Force" Test Method. Less than 1 weight percent of acetic acid was included in each composition. Each of the forming size compositions had about 2.5 weight percent solids. Each coated glass fiber strand was twisted to form a yarn and

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wound onto bobbins in a similar manner using conventional twisting equipment. Sample B<sub>vac</sub> was coated with aqueous forming size composition B, but vacuum dried at a temperature of 190°F for about 46 hours. Samples A-F each had loss on ignition values of less than 1 weight percent. Samples C<sub>hi</sub> and D<sub>hi</sub> had loss on ignition values of 1.59 and 1.66 weight percent, respectively.

**Table 1A**

COMPONENT	WT. PERCENT COMPONENT ON TOTAL SOLIDS BASIS					
	A	B	C	D	E	F
Thermoplastic polyester film-forming polymer <sup>82</sup>	28.6	29.1	31.58	50.71	0	0
Thermoplastic polyester film-forming polymer <sup>83</sup>	43.7	39.1	0	0	0	0
Epoxy film-forming polymer <sup>84</sup>	0	0	21.05	0	0	0
Epoxy film-forming polymer <sup>85</sup>	0	0	0	0	16.12	63.54
Polyvinyl pyrrolidone <sup>86</sup>	0	9.7	15.79	15.21	1.31	5.18
epoxy-functional organo silane coupling agent <sup>87</sup>	2.3	2.3	8.42	8.11	3.17	12.51
acrylic-functional organo silane coupling agent <sup>88</sup>	4.7	4.8	0	0	0	0
amino-functional organo silane coupling agent <sup>89</sup>	0	0	8.42	8.11	0	0
polyoxyalkylene block copolymer <sup>90</sup>	10.7	5.6	0	0	0	0
Ethoxylated octylphenoxyethanol <sup>91</sup>	0	0	4.74	6.39	1.63	6.44
polyamide <sup>92</sup>	4.8	4.8	0	0	0	0
Polyoxyethylated vegetable oil <sup>93</sup>	0	0	0	0	1.63	6.44
polyethylene glycol monolaurate ester <sup>94</sup>	0	0	0	0	0.79	3.11
surfactant <sup>95</sup>	3.6	3.6	4.74	6.39	0	0
Organic lubricant <sup>96</sup>	0	0	0	0	0.40	1.56

82 RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio.

83 DESMOPHEN 2000 polyethylene adipate diol which is commercially available from Bayer of Pittsburgh, Pennsylvania.

84 EPI-REZ® 3522-W-66 which is commercially available from Shell Chemical Co. of Houston, Texas.

85 EPON 826 which is commercially available from Shell Chemical of Houston, Texas.

86 PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, New Jersey.

87 A-187 gamma-glycidoxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

88 A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

89 A-1100 amino-functional organo silane coupling agent which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

90 PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey.

91 IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey.

92 VERSAMID 140 polyamide which is commercially available from General Mills Chemicals, Inc.

93 ALKAMULS EL-719 polyoxyethylated vegetable oil which is commercially available from Rhone-Poulenc.

94 KESSCO PEG 600 polyethylene glycol monolaurate ester which is commercially available from Stepan Company of Chicago, Illinois.

95 MACOL NP-6 nonylphenol surfactant which is commercially available from BASF of Parsippany, New Jersey.

96 EMERY® 6717 partially amidated polyethylene imine which is commercially available from Henkel Corporation of Kankakee, Illinois.

Organic lubricant <sup>97</sup>	0	0	4.21	4.06	0	0
polyoxyethylene polymer <sup>98</sup>	0.6	0	0	0	0	0
boron nitride powder particles <sup>99</sup>	1.0	1.0	0	0	74.78	1.00
boron nitride particles in aqueous suspension <sup>100</sup>	0	0	1.05	1.01	0	0

Commercial samples of 631 and 633 D-450 starch-oil coated yarns; 690 and 695 starch-oil coated yarns and 1383 G-75 yarns which are commercially available from PPG Industries, Inc. were also evaluated using the "Air Jet Transport Drag Force" Test Method. Three Comparative Samples X1, X2 and X3, each coated with the same aqueous forming composition X set forth in Table 1B below, were also tested. Comparative Sample X1 had 2.5 weight percent solids. Comparative Sample X2 had 4.9 weight percent solids and was air dried for about 8 hours at about 25°C. Comparative Sample X3 had 4.6 weight percent solids.

**Table 1B**

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS
	SAMPLE NO. X
Thermoplastic polyester film-forming polymer <sup>101</sup>	28.9
Thermoplastic polyester film-forming polymer <sup>102</sup>	44.1
epoxy-functional organo silane coupling agent <sup>103</sup>	2.3
acrylic-functional organo silane coupling agent <sup>104</sup>	4.8
polyoxyalkylene block copolymer <sup>105</sup>	10.9

<sup>97</sup> EMERY® 6760 lubricant which is commercially available from Henkel Corporation of Kankakee, Illinois.

<sup>98</sup> POLYOX WSR-301 polyoxyethylene polymer which is commercially available from Union Carbide of Danbury, Connecticut.

<sup>99</sup> PolarTherm® PT 160 boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio.

<sup>100</sup> ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride particles in aqueous dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee.

<sup>101</sup> RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio.

<sup>102</sup> DESMOPHEN 2000 polyethylene adipate diol which is commercially available from Bayer of Pittsburgh, Pennsylvania.

<sup>103</sup> A-187 gamma-glycidioxypropyltrimethoxysilane which is commercially available from OSI Specialties, Inc. of Tarrytown, New York.

<sup>104</sup> A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSI Specialties, Inc. of Tarrytown, New York.

<sup>105</sup> PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey.

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polyamide <sup>106</sup>	4.8
surfactant <sup>107</sup>	3.6
polyoxyethylene polymer <sup>108</sup>	0.6

Each yarn sample was fed at a rate of 274 meters (300 yards) per minute through a Sulzer Ruti needle air jet nozzle unit Model No. 044 455 001 which had an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters (commercially available from Sulzer Ruti of Spartanburg, North Carolina) at an air pressure of 310 kiloPascals (45 pounds per square inch) gauge. A tensiometer was positioned in contact with the yarn at a position prior to the yarn entering the air jet nozzle. The tensiometer provided measurements of the gram force (drag force) exerted upon each yarn sample by the air jet as the respective yarn sample was pulled into the air jet nozzle. These values are set forth in Table 1C below.

15

**Table 1C**

Sample No.	Yarn Type	loss on ignition (%)	Drag Force (gramforce)	Air Jet Transport Drag Force (gramforce per grammass)
A	G-75	0.35	68.5	103,474
B	G-75	0.30	84.9	128,248
Bvac	G-75	0.35	95.0	143,587
C	D-450	0.52	37.33	278,582
D	D-450	0.40	47.1	351,493
E	G-75	0.35	79.3	119,789
F	G-75	0.35	83.2	125,680
Comparative Samples				
631*	D-450	1.6	21.45	160,075
633*	D-450	1.3	38.1	284,328
690*	G-75	1.0	108.23	163,489
695*	G-75	1.0	100.46	151,752
1383	G-75	0.75	14.47	21,858
X1	G-75	0.33	36.4	54,985

<sup>106</sup> VERSAMID 140 polyamide which is commercially available from General Mills Chemicals, Inc.

<sup>107</sup> MACOL NP-6 nonylphenol surfactant which is commercially available from BASF of Parsippany, New Jersey.

<sup>108</sup> POLYOX WSR-301 polyoxyethylene polymer which is commercially available from Union Carbide of Danbury, Connecticut.

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X3	D-450	1.37	12.04	89,851
Chi	D-450	1.59	9.00	67,164
Dhi	D-450	1.66	10.43	77,836

\* Coated with starch-oil sizing formulations.

As shown in Table 1C above, each of the yarns coated with polymeric matrix material compatible sizing compositions according to the present invention had Air Jet Transport Drag Values greater than 100,000. Only the starch-oil sized commercial strands, which are generally incompatible with the polymeric matrix materials discussed above, had Air Jet Transport Drag Values greater than 100,000. Sample yarns C<sub>hi</sub> and D<sub>hi</sub>, which had polymeric matrix compatible coatings, had Air Jet Transport Drag Values less than 100,000 because of high coating levels on the yarns, i.e., loss on ignition greater than about 1.5%, which inhibited filamentization of the yarn by the air jet.

To evaluate laminate strength, 7628 style fabrics (style parameters discussed above) were formed from samples of 695, Sample B and Sample B<sub>vac</sub> G-75 yarns (discussed above), respectively. Eight plies of each fabric sample were laminated with a FR-4 resin system of EPON 1120-A80 epoxy resin, dicyandiamide, 2-methylimidazole and DOWANOL PM to form laminates.

Each laminate was evaluated for flexural strength (maximum failure stress) testing according to ASTM D-790 and IPC-TM-650 Test Methods Manual of the Institute for Interconnecting and Packaging Electronics (December 1994) (which are hereby incorporated by reference) with metal cladding completely removed by etching according to section 3.8.2.4 of IPC-4101 and for interlaminar shear strength (short beam shear strength) using a 15.9 millimeter (5/8th inch) span and crosshead speed of 1.27 millimeters (0.05 inches) per minute according to ASTM D-2344, which are hereby

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incorporated by reference. The results of these evaluations are shown in Table 1D below.

**Table 1D**

Sample	Flexural Strength		Flexural Modulus		Short Beam Shear Strength	
	Pascals	psi	Pascals	psi	Pascals	psi
B	$4.9 \times 10^8$	71534	$2.4 \times 10^{10}$	3465000	$2.6 \times 10^7$	3742
B <sub>vac</sub>	$5.0 \times 10^8$	72215	$2.4 \times 10^{10}$	3450600	$2.5 \times 10^7$	3647
695	$4.3 \times 10^8$	62959	$2.3 \times 10^{10}$	3360800	$2.3 \times 10^7$	3264

5

As shown in Table 1D, Laminate Samples B and B<sub>vac</sub> prepared according to the present invention had higher flexural strength and modulus values and similar short beam shear strength when compared to laminate samples prepared from 695 starch-oil coated glass fiber yarn.

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**EXAMPLE 2**

The coefficient of thermal expansion in the z-direction of the laminate ("Z-CTE"), i.e., across the thickness of the laminate, was evaluated for laminate samples, each containing eight layers of 7628 style fabric prepared from samples of B<sub>vac</sub> coated yarn (Sample A) and 695 starch-oil coated yarns (discussed above) (Control). The laminate was prepared using the FR-4 epoxy resin discussed in Example 1 above and clad with copper according to IPC Test Method 2.4.41, which is hereby incorporated by reference. The coefficient of thermal expansion in the z-direction was evaluated for each laminate sample at 288°C according to IPC Test Method 2.4.41. The results of the evaluations are shown in Table 2 below.

20



**Table 2**

Sample	Z-CTE (%)
Sample A1	4.10
Sample A1 (retest)	4.41
Sample A2	4.06
Sample A2 (retest)	4.28
Sample A3	4.17
Sample A3 (retest)	4.26
Control 1	5.0
Control 2	5.4

As shown in Table 2, for laminate Samples A1-A3 according to the present invention, the coefficients of thermal expansion in the z-direction of the laminates are less than those of Control Samples 1 and 2, which were  
5 prepared from 695 starch-oil coated yarn.

**EXAMPLE 3**

Aqueous forming size compositions A-D (discussed in Table 1A, Example 1 above) and Comparative Sample No. 1 were coated onto E-glass  
10 fiber strands. The formulation for Comparative Sample No. 1 is set forth in Table 3 below. Each of the forming size compositions had about 2.5 weight percent solids. Each coated glass fiber strand was twisted to form a yarn and wound onto bobbins in a similar manner using conventional twisting  
15 equipment.

**Table 3**

	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS
	SAMPLE NO.
COMPONENT	Comp. Sample No. 1
Thermoplastic polyester film-forming polymer <sup>109</sup>	28.9
Thermoplastic polyester film-forming polymer <sup>110</sup>	44.1
epoxy-functional organo silane coupling agent <sup>111</sup>	2.3
acrylic-functional organo silane coupling agent <sup>112</sup>	4.8
polyoxyalkylene block copolymer <sup>113</sup>	10.9
polyamide <sup>114</sup>	4.8
surfactant <sup>115</sup>	3.6
polyoxyethylene polymer <sup>116</sup>	0.6

The yarns of Samples A-D, Comparative Sample No. 1 and a Comparative Sample No. 2<sup>117</sup> were evaluated for several physical properties, such as loss on ignition (LOI), air jet compatibility (Air Drag), Friction Force and broken filaments.

The average loss on ignition (weight percent of solids of the forming size composition divided by the total weight of the glass and dried forming size composition) of three trials of each Sample is set forth in Table 4.

Each yarn was evaluated for Air Drag Force or tension by feeding the yarn at a controlled feed rate of 274 meters (300 yards) per minute through a checkline tension meter, which applied a tension to the yarn, and a Ruti two

<sup>109</sup> RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio.

<sup>110</sup> DESMOPHEN 2000 polyethylene adipate diol which is commercially available from Bayer of Pittsburgh, Pennsylvania.

<sup>111</sup> A-187 gamma-glycidioxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

<sup>112</sup> A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.

<sup>113</sup> PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey.

<sup>114</sup> VERSAMID 140 polyamide which is commercially available from General Mills Chemicals, Inc.

<sup>115</sup> MACOL NP-6 nonylphenol surfactant which is commercially available from BASF of Parsippany, New Jersey.

<sup>116</sup> POLYOX WSR-301 polyoxyethylene polymer which is commercially available from Union Carbide of Danbury, Connecticut.

<sup>117</sup> PPG Industries, Inc.'s 1383 commercially available fiber glass yarn product.

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millimeter diameter air nozzle at an air pressure of 310 kPa (45 pounds per square inch).

The Samples and Comparative Samples were also evaluated for Friction Force by applying a tension of about 30 grams to each yarn sample  
5 as the sample is pulled at a rate of 274 meters (300 yards) per minute through a pair of conventional tension measurement devices having a stationary chrome post of about 5 centimeters (2 inches) diameter mounted therebetween to displace the yarn about 5 centimeters from a straight line path between the tension measurement devices. The difference in force in  
10 grams is set forth in Table 4 below. The Friction Force test is intended to simulate the frictional forces to which the yarn is subjected during weaving operations.

Each sample and comparative sample was also evaluated for broken filaments using an abrasion tester. Two hundred grams of tension were  
15 applied to each test sample as each test sample was pulled at a rate of 0.46 meters (18 inches) per minute for five minutes through an abrasion testing apparatus. Two test runs of each sample and comparative sample were evaluated and the average of the number of broken filaments is reported in Table 4 below. The abrasion tester consisted of two parallel rows of steel  
20 reeds, each row being positioned about 1 inch apart. Each test yarn sample was threaded between two adjacent reeds of the first row of reeds, then threaded between two adjacent reeds of the second row of reeds, but displaced a distance of one-half inch between the rows of reeds. The reeds were displaced back and forth over a four inch length in a direction parallel to  
25 the direction of yarn travel at a rate of 240 cycles per minute. The results of Air Drag Force, Friction Force and Broken Filaments Under Abrasion for Samples A-D and the comparative samples are set forth in Table 4 below.

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**Table 4**

	Sample					
	A	B	C	D	Comparative Sample No. 1	Comparative Sample No. 2
LOI (weight percent)	0.35	0.30	0.52	0.40	0.33	0.75
Air Drag (grams)	68.5	84.9	37.3	47.1	36.4	19.0
Friction force (grams)	24.7	18.3	-	-	23.9	38.1
Number of broken filaments per yard of yarn	2.0	1.0	-	-	3.8	1.0

As shown in Table 4, Samples A and B, which are coated with sizing compositions containing boron nitride according to the present invention, had few broken filaments, low frictional force and higher air drag values when compared to the Comparative Samples. Samples C and D also had higher air drag values than the Comparative Samples. The air drag test is a relative test intended to simulate the weft insertion process of an air jet loom in which the yarn is conveyed across the loom by air jet propulsion. Yarns which are more readily filamentized by the air jet provide greater surface area for air jet propulsion, which can facilitate yarn travel across the loom and increase productivity. The air drag values for Samples A-D (samples prepared according to the present invention) are higher than those of the Comparative Samples, which indicates superior air jet compatibility.

**EXAMPLE 4**

Each of the components in the amounts set forth in Table 5 were mixed to form aqueous forming size compositions E, F, G and H according to the present invention and the Comparative Sample in a similar manner to that discussed above. Less than about 1 weight percent of acetic acid on a total weight basis was included in each composition.

Each of the aqueous forming size compositions of Table 5 were coated onto G-75 E-glass fiber strands. Each of the forming size compositions had between about 6 and about 25 weight percent solids.

5

**Table 5**

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS				
	Sample No.				
	E	F	G	H	Comp. Sample
Epoxy film-forming polymer <sup>118</sup>	16.12	63.54	16.12	63.54	60.98
Polyvinyl pyrrolidone <sup>119</sup>	1.31	5.18	1.31	5.18	4.97
Polyoxyethylated vegetable oil <sup>120</sup>	1.63	6.44	1.63	6.44	6.18
Ethoxylated octylphenoxyethanol <sup>121</sup>	1.63	6.44	1.63	6.44	6.18
polyethylene glycol monolaurate ester <sup>122</sup>	0.79	3.11	0.79	3.11	2.98
Epoxy-functional organo silane coupling agent <sup>123</sup>	3.17	12.51	3.17	12.51	12.00
Organic lubricant <sup>124</sup>	0.40	1.56	0.40	1.56	1.50
polyethylene emulsion <sup>125</sup>	0	0	0	0	4.61
Boron nitride powder particles <sup>126</sup>	74.78	1.00	0	0	0
Boron nitride particles in aqueous suspension <sup>127</sup>	0	0	74.78	1.00	0

118 EPON 826 which is commercially available from Shell Chemical of Houston, Texas.

119 PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, New Jersey.

120 ALKAMULS EL-719 polyoxyethylated vegetable oil which is commercially available from Rhone-Poulenc.

121 IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey.

122 KESSCO PEG 600 polyethylene glycol monolaurate ester which is commercially available from Stepan Company of Chicago, Illinois.

123 A-187 gamma-glycidoxypropyltrimethoxysilane which is commercially available from OSI Specialties, Inc. of Tarrytown, New York.

124 EMERY® 6717 partially amidated polyethylene imine which is commercially available from Henkel Corporation of Kankakee, Illinois.

125 Protolube HD high density polyethylene emulsion which is commercially available from Sybron Chemicals of Birmingham, New Jersey.

126 PolarTherm® PT 160 boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio.

127 ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride particles in aqueous dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee.

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Each coated glass fiber strand was twisted to form yarn and wound onto bobbins in a similar manner using conventional twisting equipment. The yarns of Samples F and H exhibited minimal sizing shedding during twisting and the yarns of Samples E and G exhibited severe sizing shedding during  
5 twisting.

The yarns of Samples E-H and Comparative Sample were evaluated for Air Drag in a similar manner to Example 3 above, except that the Air Drag values were determined for two bobbin samples at the pressures indicated in Table 6. Each yarn was evaluated for average number of broken filaments  
10 per 1200 meters of yarn at 200 meters per minute using a Shirley Model No. 84 041L broken filament detector, which is commercially available from SDL International Inc. of England. These values represent the average of measurements conducted on four bobbins of each yarn. The broken filament values are reported from sections taken from a full bobbin, 136 grams (3/10  
15 pound) and 272 grams (6/10 pound) of yarn unwound from the bobbin.

Each yarn was also evaluated for Gate Tension testing are set forth in Table 6 below. The number of broken filaments measured according to the Gate Tension Method is determined by unwinding a sample of yarn from a bobbin at 200 meters/minute, threading the yarn through a series of 8 parallel  
20 ceramic pins and passing the yarn through the Shirley broken filament detector discussed above to count the number of broken filaments.

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**TABLE 6**

NUMBER OF BROKEN FILAMENTS PER METER OF YARN		Sample E	Sample F	Sample G	Sample H	Comp. Sample
full bobbin		0.887	0.241	greater than 10	0.065	0.192
136 grams (3/10 pound)		0.856	0.017	greater than 10	0.013	0.320
272 grams (6/10 pound)		0.676	0.030	greater than 10	0.101	0.192
GATE TENSION (number of hairs per meter)						
Gate 2		-	0.039	-	0.0235	0.721
Gate 3		-	0.025	-	0.028	0.571
Gate 4		-	0.0125	-	0.068	0.4795
Gate 5		-	0.015	-	0.093	0.85
Gate 6		-	0.0265	-	0.118	0.993
Gate 7		-	0.0695	-	0.31	1.0835
Gate 8		-	0.117	-	0.557	1.81
AIR DRAG (grams)						
25 psi	Bobbin 1	-	10.420	-	10.860	11.610
	Bobbin 2	-	10.600	-	7.850	11.610
30 psi	Bobbin 1	-	11.690	-	12.500	13.680
	Bobbin 2	-	12.200	-	8.540	13.850
35 psi	Bobbin 1	-	13.490	-	14.030	15.880
	Bobbin 2	-	13.530	-	9.570	15.630
40 psi	Bobbin 1	-	14.740	-	14.110	17.560
	Bobbin 2	-	14.860	-	11.010	17.610
45 psi	Bobbin 1	-	16.180	-	16.390	19.830
	Bobbin 2	-	16.680	-	12.700	18.950
50 psi	Bobbin 1	-	17.510	-	19.280	22.410
	Bobbin 2	-	17.730	-	14.000	20.310
55 psi	Bobbin 1	-	19.570	-	23.350	29.350
	Bobbin 2	-	19.660	-	20.250	26.580

While the test results presented in Table 6 appear to indicate that Samples E-H according to the present invention had generally higher abrasion resistance than the Comparative Sample, it is believed that these results are not conclusive since it is believed that a polyethylene emulsion component of the Comparative Sample, which was not present in Samples E-H, contributed to abrasive properties of the yarn.

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From the foregoing description, it can be seen that the present invention provides laminates having good flexural strength and modulus and coefficient of thermal expansion in the z-direction, as well as other desirable advantages, which are useful in a wide variety of applications, such as

5 reinforcements for printed circuit boards.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover

10 modifications which are within the spirit and scope of the invention, as defined by the appended claims.



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## THEREFORE, WE CLAIM:

1. A reinforced laminate for an electronic support, the laminate comprising:
  - 5 (a) a polymeric matrix material; and
  - (b) a woven reinforcement fabric comprising a yarn comprising glass fibers at least partially coated with a coating which is compatible with the polymeric matrix material, the yarn having a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force  
10 of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge,  
15 wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi).
2. The reinforced laminate according to claim 1, wherein the polymeric matrix material comprises at least one material selected from the  
20 group consisting of thermosetting matrix materials and thermoplastic matrix materials.
3. The reinforced laminate according to claim 2, wherein the polymeric matrix material comprises at least one thermosetting matrix  
25 material selected from the group consisting of thermosetting polyesters, vinyl esters, epoxides, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof.

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4. The reinforced laminate according to claim 3, wherein the thermosetting matrix material comprises an epoxide.

5. The reinforced laminate according to claim 2, wherein the  
5 polymeric matrix material comprises at least one thermoplastic matrix material selected from the group consisting of polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, vinyl polymers, polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polycarbonates and mixtures thereof.

10

6. The reinforced laminate according to claim 1, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

15

7. The reinforced laminate according to claim 6, wherein the at least one of the glass fibers is an E-glass fiber.

8. The reinforced laminate according to claim 6, wherein the at  
20 least one of the glass fibers is an E-glass derivative fibers.

9. The reinforced laminate according to claim 1, wherein the coating upon the glass fibers of the fabric comprises inorganic solid lubricant particles.

25

10. The reinforced laminate according to claim 9, wherein the inorganic solid lubricant particles of the coating have a lamellar structure.

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11. The reinforced laminate according to claim 9, wherein the inorganic solid lubricant particles comprise at least one particle selected from the group consisting of non-hydratable inorganic solid lubricant particles, hydratable inorganic solid lubricant particles and mixtures thereof.

5

12. The reinforced laminate according to claim 11, wherein the non-hydratable inorganic solid lubricant particles comprise at least one particle selected from the group consisting of graphite, boron nitride, metal dichalcogenides, cadmium iodide, silver sulfide and mixtures thereof.

10

13. The reinforced laminate according to claim 12, wherein the non-hydratable inorganic solid lubricant particles comprise hexagonal crystal structure boron nitride particles.

15

14. The reinforced laminate according to claim 12, wherein the non-hydratable inorganic solid lubricant particles comprise at least one metal dichalcogenide selected from the group consisting of molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

20

15. The reinforced laminate according to claim 11, wherein the non-hydratable inorganic solid lubricant particles comprise at least one particle selected from the group consisting of indium, thallium, tin, copper, zinc, gold, silver, calcium carbonate, calcium fluoride, zinc oxide and mixtures thereof.

25

16. The reinforced laminate according to claim 11, wherein the hydratable inorganic solid lubricant particles comprise phyllosilicates.

17. The reinforced laminate according to claim 16, wherein the phyllosilicates comprise at least one phyllosilicate selected from the group consisting of mica, talc, gypsum, kaolinite, montmorillonite and mixtures thereof.

5

18. The reinforced laminate according to claim 11, wherein a hardness value of the inorganic solid lubricant particles is less than or equal to a hardness value of the E-glass fibers.

10

19. The reinforced laminate according to claim 1, wherein the coating upon the glass fibers of the fabric comprises a film-forming polymer.

15

20. The reinforced laminate according to claim 1, wherein at least one of the glass fibers is formed from a fiberizable material selected from the group consisting of non-glass inorganic materials, natural materials, organic polymeric materials and combinations thereof.

20

21. The reinforced laminate according to claim 1, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $4.9 \times 10^7$  kilograms per square meter (about 70 kpsi).

22. A reinforced laminate for an electronic support, the laminate comprising:

25

- (a) a polymeric matrix material; and
- (b) a woven reinforcement fabric comprising a yarn comprising glass fibers at least partially coated with a coating which is compatible with the polymeric matrix material, the coating comprising (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches.

23. The reinforced laminate according to claim 22, wherein the polymeric matrix material comprises at least one material selected from the group consisting of thermosetting matrix materials and thermoplastic matrix materials.

24. The reinforced laminate according to claim 23, wherein the polymeric matrix material comprises at least one thermosetting matrix material selected from the group consisting of thermosetting polyesters, vinyl esters, epoxides, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof.

25. The reinforced laminate according to claim 24, wherein the thermosetting matrix material comprises an epoxide.

26. The reinforced laminate according to claim 23, wherein the polymeric matrix material is a thermoplastic matrix material selected from the group consisting of polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, vinyl polymers, polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polycarbonates and mixtures thereof.

27. The reinforced laminate according to claim 22, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

28. The reinforced laminate according to claim 27, wherein the at least one of the glass fibers is an E-glass fiber.

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29. The reinforced laminate according to claim 27, wherein the at least one of the glass fibers is an E-glass derivative fibers.

5           30. The reinforced laminate according to claim 22, wherein the coating upon the glass fibers of the fabric further comprises inorganic solid lubricant particles.

31. The reinforced laminate according to claim 30, wherein the  
10 inorganic solid lubricant particles of the coating have a lamellar structure.

32. The reinforced laminate according to claim 30, wherein the inorganic solid lubricant particles comprise at least one particle selected from the group consisting of non-hydratable inorganic solid lubricant particles,  
15 hydratable inorganic solid lubricant particles and mixtures thereof.

33. The reinforced laminate according to claim 32, wherein the non-hydratable inorganic solid lubricant particles comprises at least one particle selected from the group consisting of graphite, boron nitride, metal  
20 dichalcogenides, cadmium iodide, silver sulfide and mixtures thereof.

34. The reinforced laminate according to claim 33, wherein the non-hydratable inorganic solid lubricant particles comprise hexagonal crystal structure boron nitride particles.  
25

35. The reinforced laminate according to claim 33, wherein the non-hydratable inorganic solid lubricant particles comprises at least one metal dichalcogenide selected from the group consisting of molybdenum disulfide,

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molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

36. The reinforced laminate according to claim 32, wherein the non-  
5 hydratable inorganic solid lubricant particles comprises at least one particle selected from the group consisting of indium, thallium, tin, copper, zinc, gold, silver, calcium carbonate, calcium fluoride, zinc oxide and mixtures thereof.

37. The reinforced laminate according to claim 32, wherein the  
10 hydratable inorganic solid lubricant particles comprise phyllosilicates.

38. The reinforced laminate according to claim 37, wherein the  
phyllosilicates comprise at least one phyllosilicate selected from the group  
consisting of mica, talc, gypsum, kaolinite, montmorillonite and mixtures  
15 thereof.

39. The reinforced laminate according to claim 30, wherein a  
hardness value of the inorganic solid lubricant particles is less than or equal  
to a hardness value of the glass fibers.

20

40. The reinforced laminate according to claim 22, wherein the  
coating upon the E-glass fibers of the fabric comprises a film-forming polymer.

41. The reinforced laminate according to claim 22, wherein at least  
25 one of the glass fibers is formed from a fiberizable material selected from the group consisting of non-glass inorganic materials, natural materials, organic polymeric materials and combinations thereof.

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42. The reinforced laminate according to claim 22, wherein the yarn has a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an  
5 internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge.

10 43. The reinforced laminate according to claim 22, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi).

44. A reinforced laminate for an electronic support, the laminate  
15 comprising:  
    (a) a polymeric matrix material; and  
    (b) a woven reinforcement fabric comprising a yarn comprising glass fibers at least partially coated with a coating which is compatible with the polymeric matrix material, the coating comprising (1) polyester; and (2)  
20 vinyl pyrrolidone polymer.

45. The reinforced laminate according to claim 44, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and  
25 combinations thereof.



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46. An electronic circuit board comprising:
- (a) a laminate for an electronic support comprising:
- (i) a woven fabric comprising a yarn comprising glass fibers, the yarn having a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi); and
- (ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and
- (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the laminate.

47. The electronic circuit board according to claim 46, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

48. The electronic circuit board according to claim 46 further comprising at least one aperture extending through at least a portion of the circuit board.

49. The electronic circuit board according to claim 46 wherein the circuit board is a first, second or third level package.

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50. An electronic circuit board comprising:

(a) a laminate for an electronic support comprising:

(i) a woven fabric comprising a yarn comprising glass fibers at least partially coated with a coating comprising (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches; and

(ii) a layer of a polymeric matrix material applied over at least a portion of the fabric; and

(b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the laminate.

51. The electronic circuit board according to claim 50, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

52. The electronic circuit board according to claim 50 further comprising at least one aperture extending through at least a portion of the circuit board.

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53. The electronic circuit board according to claim 50 wherein the circuit board is a first, second or third level package.

54. An electronic circuit board comprising:

(a) a laminate for an electronic support comprising:

(i) a first composite layer comprising:

(1) a woven fabric comprising a yarn comprising glass fibers, the yarn having a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about

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- 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310
- 5 kiloPascals (about 45 pounds per square inch) gauge, wherein the laminate has a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi); and
- (2) a layer of a polymeric matrix material applied over at least a portion of the fabric; and
- 10 (ii) a second composite layer different from the first composite layer; and
- (b) an electrically conductive layer positioned adjacent to selected portions of selected sides of the laminate.

- 15 55. The electronic circuit board according to claim 54, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

- 20 56. The electronic circuit board according to claim 54 further comprising at least one aperture extending through at least a portion of the circuit board.

57. The electronic circuit board according to claim 54 wherein the  
25 circuit board is a first, second or third level package.

58. An electronic circuit board comprising:

- (a) a laminate for an electronic support comprising:  
(i) a first composite layer comprising:

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- (1) a woven fabric comprising a yarn comprising glass fibers at least partially coated with a coating comprising (A) polyester; and (B) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches; and
- 5 (2) a layer of a polymeric matrix material applied over at least a portion of the fabric; and
- (ii) a second composite layer different from the first composite layer; and
- (b) an electrically conductive layer positioned adjacent to selected
- 10 portions of selected sides of the laminate.

59. The electronic circuit board according to claim 58, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers,

15 and combinations thereof.

60. The electronic circuit board according to claim 58 further comprising at least one aperture extending through at least a portion of the circuit board.

20

61. The electronic circuit board according to claim 58 wherein the circuit board is a first, second or third level package.

62. A copper-clad reinforced laminate for an electronic support, the

25 laminate comprising:

- (a) a polymeric matrix material; and
- (b) one or more plies of woven reinforcement fabric, each of the plies comprising between about 30 and about 75 weight percent of yarn comprising glass fibers at least partially coated with a coating which is

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compatible with the polymeric matrix material, wherein the laminate has a coefficient of thermal expansion in the z-direction of less than about 4.5 percent at a temperature of 288°C.

- 5           63.    The laminate according to claim 62, wherein the laminate has a coefficient of thermal expansion in the z-direction ranging from about 1 to about 4.5 percent at a temperature of 288°C.

- 10           64.    The laminate according to claim 62, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

- 15           65.    The laminate according to claim 62 further comprising at least one aperture extending through at least a portion of the circuit board.

66.    The laminate according to claim 62 wherein the circuit board is a first, second or third level package.

- 20           67.    The laminate according to claim 62 wherein the laminate comprises eight plies of 7628 style woven fabric.

68.    A method for assembling a fabric by interweaving a first yarn with a second yarn to form a fabric, wherein the improvement comprises:  
25   the first yarn comprising glass fibers at least partially coated with a coating which is compatible with a polymeric matrix material, the coating comprising: (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers, starches and mixtures thereof.

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69. The method according to claim 68, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

70. A method for forming a laminate of a woven fabric and a polymeric matrix material by at least partially coating the woven fabric with the polymeric matrix material to form a coated fabric and applying heat to the coated fabric, the woven fabric comprising a yarn comprising glass fibers, wherein the improvement comprises:

the glass fibers being at least partially coated with a coating which is compatible with the polymeric matrix material, the yarn having a loss on ignition ranging from about 0.01 to about 0.6 weight percent and an Air Jet Transport Drag Force of greater than about 100,000 gram force per gram mass of yarn using a needle air jet nozzle unit having an internal air jet chamber having a diameter of 2 millimeters and a nozzle exit tube having a length of 20 centimeters at a yarn feed rate of about 274 meters (about 300 yards) per minute and an air pressure of about 310 kiloPascals (about 45 pounds per square inch) gauge, and the laminate having a flexural strength in the fill direction of the fabric greater than about  $3 \times 10^7$  kilograms per square meter (about 42.7 kpsi).

71. The method according to claim 70, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

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72. A method for forming a laminate of a woven fabric and a polymeric matrix material by at least partially coating the woven fabric with the polymeric matrix material to form a coated fabric and applying heat to the coated fabric, the woven fabric comprising a yarn comprising glass fibers,

5 wherein the improvement comprises:

the glass fibers being at least partially coated with a coating which is compatible with a polymeric matrix material, the coating comprising: (1) polyester; and (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches.

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73. The laminate according to claim 72, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

15

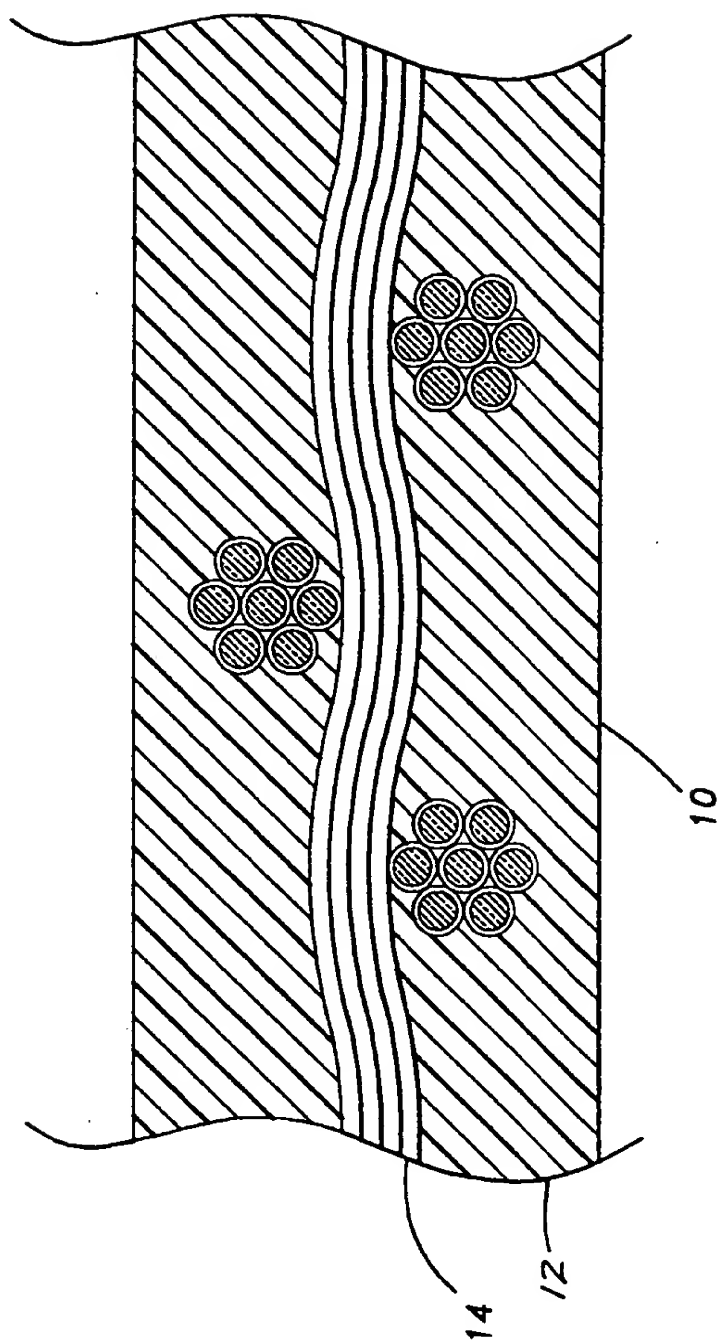


FIG. 1



2 / 5

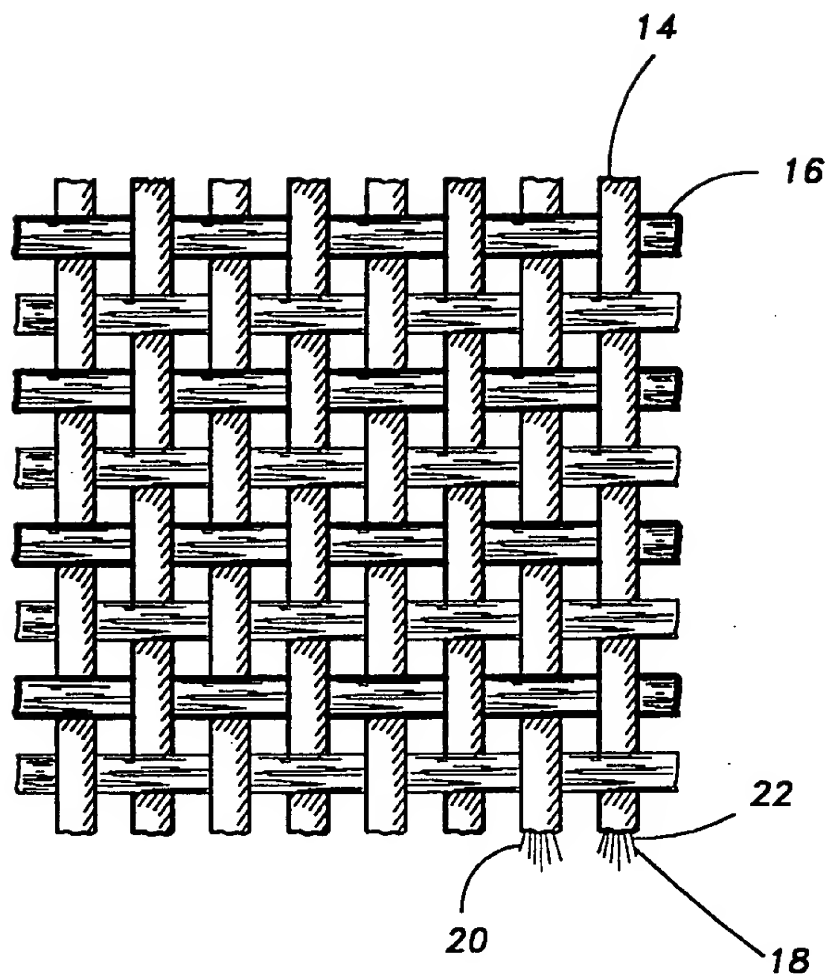


FIG. 2

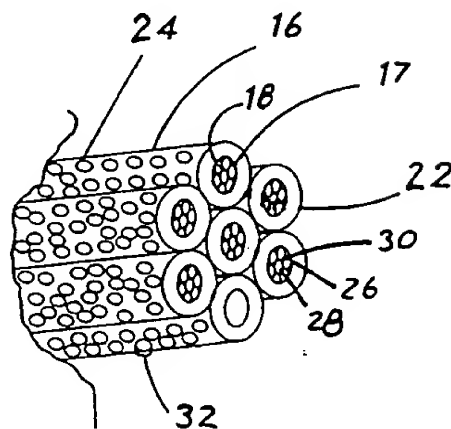


FIG. 3

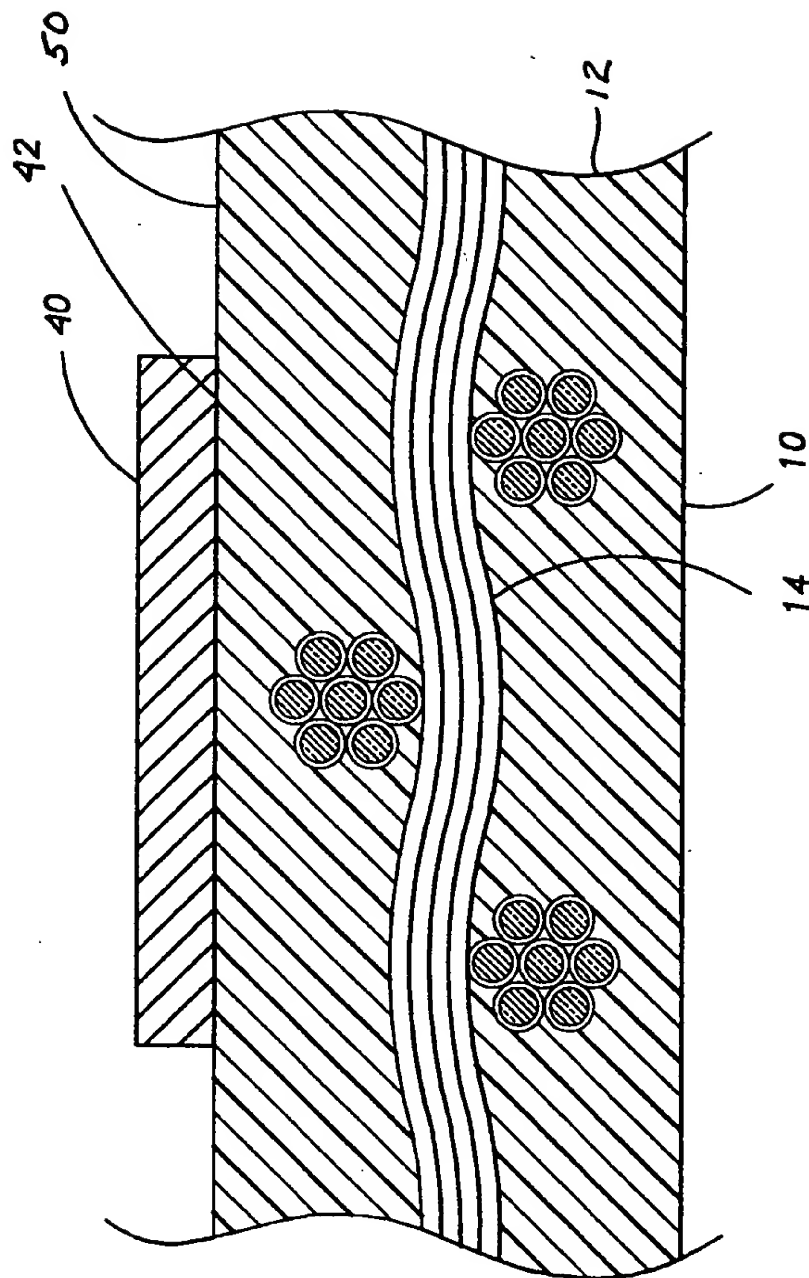


FIG. 4

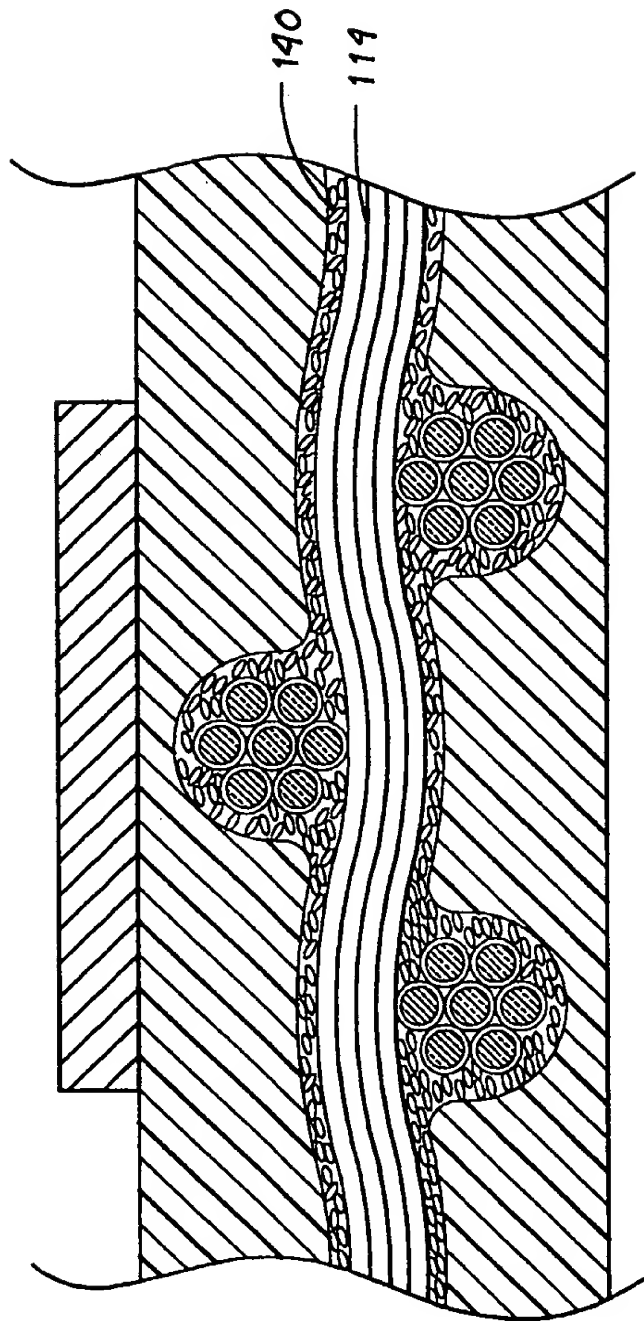


FIG. 5

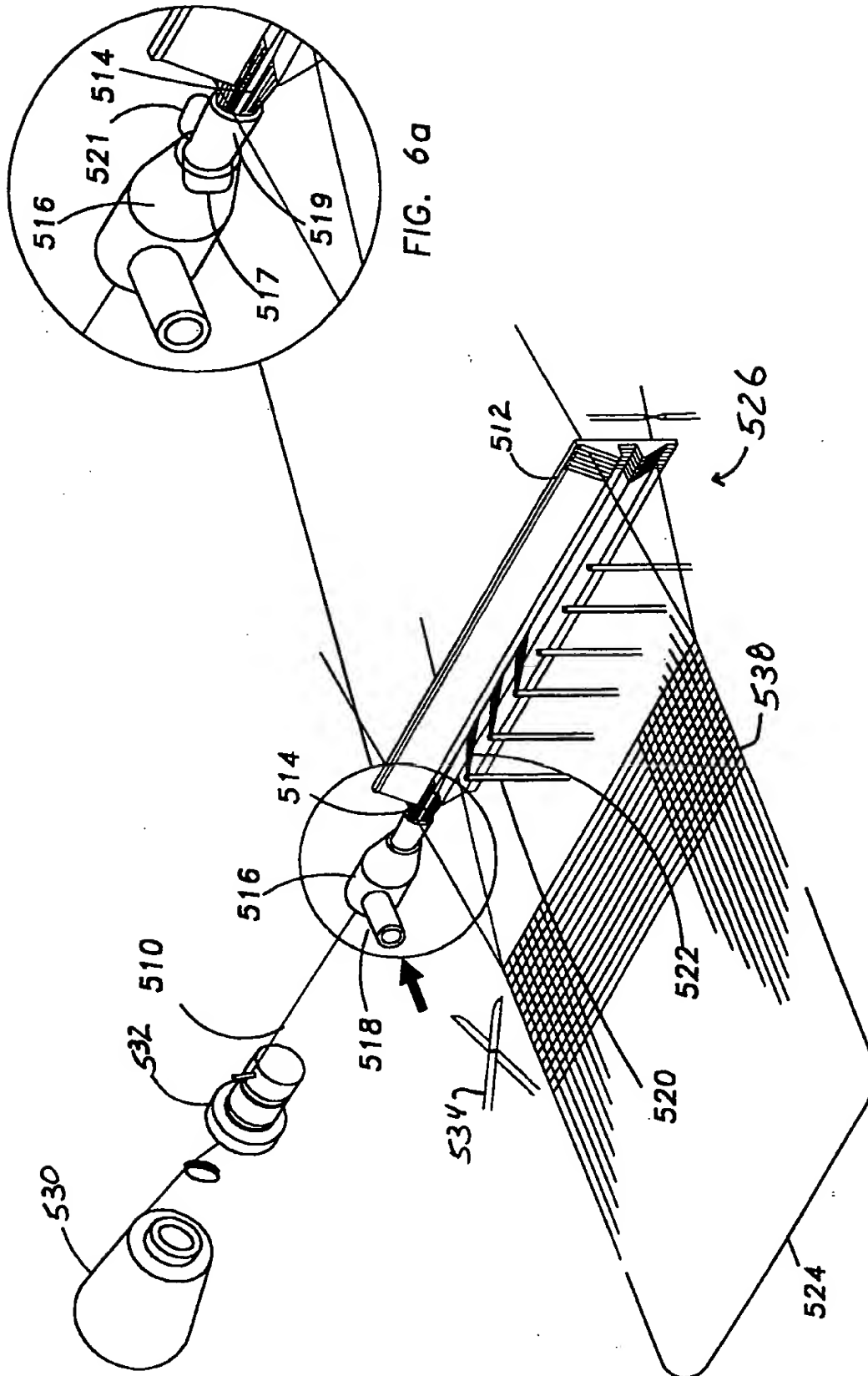


FIG. 6

FIG. 6a

## INTERNATIONAL SEARCH REPORT

Inter. Appl. No.

PCT/US 99/04086

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C25/02 C08J5/08 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C C08J H05K F16D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 39364 A (PPG INDUSTRIES INC.) 12 December 1996  see page 5, line 1 - line 13 ---	1-8, 19-29, 40-73
A	WO 90 01860 A (TELDIX GMBH) 22 February 1990 see claims ---	1-73
A	US 3 312 569 A (T.E. PHILIPPS ET AL.) 4 April 1967 cited in the application see claims ---	1-73
A	US 5 217 778 A (G.J. LACHASSE) 8 June 1993 cited in the application see abstract ---	1-73
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

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Date of the actual completion of the international search

18 June 1999

Date of mailing of the international search report

28/06/1999

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9706 Derwent Publications Ltd., London, GB; Class A85, AN 97-060830 XP002106571 & JP 08 309928 A (HITACHI CHEM CO LTD) , 26 November 1996 see abstract ---	1-73
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